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OIL TAGGING SYSTEM STUDY

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27 Abstract

Several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques; and it must have no adverse effect on the oil's subsequent use. Three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three methods of active tagging (halogenated polycyclic aromatics, organometallics, and coded microspheroids) have been examined. Passive tags cannot be recommended because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized; even if these processes do not occur, they can create formidable forensic problems for the prosecution and telling counter-arguments for the defense. Since active tags are designed to be stable and identifiable, they are satisfactory for the job; and the three types of active tags reviewed show promise and merit. (See also W70-04655)

~~This report was submitted in partial fulfillment of Contract Number 14-12-500 between the Federal Water Pollution Control Administration and Melpar, an American-Standard Company.~~

Abstractor

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OIL TAGGING SYSTEM STUDY

by

Research Division, Environmental
and Applied Sciences Center

MELPAR
An American-Standard Company
7700 Arlington Boulevard
Falls Church, Virginia 22046

for the
Federal Water Pollution Control Administration
Department of the Interior

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ABSTRACT

Several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques; and it must have no adverse effect on the oil's subsequent use. Three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three methods of active tagging (halogenated polycyclic aromatics, organometallics, and coded microspheroids) have been examined. Passive tags cannot be recommended because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized; even if these processes do not occur, they can create formidable forensic problems for the prosecution and telling counter-arguments for the defense. Since active tags are designed to be stable and identifiable, they are satisfactory for the job; and the three types of active tags reviewed show promise and merit.

This report was submitted in fulfillment of Contract Number 14-12-500 under the sponsorship of the Federal Water Pollution Control Administration.

Key Words: Pollutant identification, tagging, oil wastes, tracers, analytical techniques, chemical analysis, chromatography, waste identification, indicators, water pollution control, oil industry.

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SECTION I

OIL POLLUTION—THE SIZE AND SOURCE OF THE PROBLEM

Before analyzing several suggested methods for identifying spilled oil, a few words about the size and source of the oil-pollution problem are in order. How much petroleum (crude and refined) has been spilled on U.S. waters in recent years? How many spills were there? What sources were responsible? What is the potential pollution?

Authoritative (but incomplete) answers to these questions have been published in official Government documents: Congressional Hearings, reports from the Bureau of Mines, and special reports to the President and to Congress prepared by the Federal agencies that administer water-pollution laws. There are also private sources of interest. Some of the highlights are summarized in the following discussion.

The United States carries on an enormous foreign trade in petroleum and petroleum products. The U.S. Bureau of Mines has estimated[1] that in 1967 this trade came to more than 1 billion barrels (42 gallons per barrel), 90 percent of which was imports. Almost all of this trade is conducted by ship. The Bureau also reports that, of the 3.6 billion barrels of oil refined in the U.S. in 1967, about 800 million barrels were sent to the refinery over water. The volume of petroleum transported over water to U.S. coastal and inland ports each year is astronomic: It has been estimated[2] that the tonnage of petroleum moving by water is substantially greater than the combined tonnage of all other commodities. The potential for oil spills is obvious.

Although oil spills are illegal all over the world (by international convention,[3] usually supplemented by national statutes), laws are often observed only in the breach. The U.S. is no exception, even though there are at least six statutory laws that apply: the Oil Pollution Act of 1924 (33 USC 431 et seq.), the Oil Pollution Act of 1961 (33 USC 1001 et seq.), the Refuse Act of 1899 (33 USC 407), the Dangerous Cargo Act (46 USC 170), the Tank Vessel Act (46 USC 391a), and the so-called Magnuson Act (50 USC 191).[4]

In one winter, November 1, 1968, to February 22, 1969, there were over a million gallons of crude and refined petroleum spilled on U.S. waters from pipelines, offshore installations, tankers, and barges. During the same period, on January 28, 1969, Union Oil Company's well 12-A in the Santa Barbara Channel, OCSP-0241, blew out while a drill pipe was being removed. Gas and oil (300,000 bbl per day) flowed from the ocean floor near the well. It was ten days later before the well was killed.

There has been no thorough nationwide survey of the oil spilled into U.S. inland and offshore waters by vessels and barges, particularly as distinct from spills out of shore facilities. However, scattered data suggests that spill incidents are frequent, despite the fact that oil discharges into American waters are prohibited. The U.S. Army Corps of Engineers estimates that there were over 2000 oil spills within U.S. waters in 1966, of which 40 percent came from land-based facilities. Recent Federal Water Pollution Control Administration estimates indicate that illegal discharges range between 7,000 and 10,000 annually. Many of the spills, however, are unwitnessed and go unreported; then the enforcement of the oil pollution laws becomes quite a problem.

A particular problem in connection with the Oil Pollution Act of 1924, as amended, is the extreme difficulty of apprehending and prosecuting offenders at sea. The Coast Guard, for example, listed 458 violations of the oil pollution statutes detected in 1967 (of which 63 involved tankers, 56 dry cargo ships, and 56 Navy ships that reported themselves). Privately, however, Coast Guard officials suggest that the number of actual violations may have been closer to 5,000 than 500. The problem is that an oil spill, such as the one that hit Cape Cod beaches in 1967, often isn't detected until the offending ship is long out of the area. Unless a witness is on the scene when a violation occurs or a particular slick can be chemically traced to a particular ship known to have passed through a polluted area, spills go completely undetected until the oil washes up on a beach and someone complains.[7]

Maritime collisions are known to contribute to oil pollution. The Secretaries' Report to the President summarizes the most important facts:

> The maritime casualty rate, including barge casualties on the inland waters, fluctuates at a level sufficiently high to justify serious concern. The following figures summarize the recent combined casualty record of U.S.-registered vessels worldwide and foreign vessels in U.S. waters:

	FY 1966	FY 1967
Number of casualties, all types	2,408	2,353
Vessels over 1,000 tons	1,310	1,347
Tank ships and tank barges	470	499
Locations:		
U.S. waters	1,685	1,569
Elsewhere	723	784
Types of casualties:		
Collisions	922	1,090
Explosions	175	168
Groundings with damages	302	282
Founderings, capsizings, and floodings	315	230

> These types of casualties can and in some cases do cause polluting spills....[11]

To put these figures into proper perspective, it must be remembered that in 1965 the world's merchant fleet contained

> ...over 18,000 vessels of 1,000 gross tons or heavier; almost 3,500 of these vessels were tankers. Of the total, the U.S. flag was represented by about 2,500 vessels, of which approximately 400 were tankers. About 1,000 of the American vessels were regularly engaged in foreign commerce, while the remainder served in the U.S. coastwise and other domestic trades. The foregoing fleet was supplemented within the United States by approximately 36,000 smaller vessels. ...These included several thousand tank ships and tank barges on the American inland waterways.
>
> ...To illustrate the extent to which U.S. waters are used by vessels in the foreign trade, the following table sets forth the approximate numbers of visits to U.S. ports in FY 1966 by vessels over 1,000 deadweight tons:

Ship Type	Number	Average Oil Cargo Capacity (tons)	Average Bunker Oil Capacity (tons)
Foreign--Dry Cargo	34,000	*****	1,400
Foreign--Tanker	6,100	25,000	2,500
U.S.--Dry Cargo	7,000	*****	3,400
U.S.--Tanker	3,000	14,000	1,300

> In summary, there were over 50,000 visits to U.S. ports in FY 1966 by medium-size and large ocean-going vessels with a cumulative capacity of almost 300 million tons of potentially polluting materials.[12]

Oil pollution from offshore wells is not a much larger problem. According to the testimony of Dr. William T. Pecora, Director of the U.S. Geological Survey, before the Senate Committee on Public Works[8]

> There have been a total of 14,000 wells drilled off shore, both State and Federal (i.e., on State and Federal offshore lands). The Federal proportion is 10,243 wells, and the State portion is 3,847 wells...[14]

Land-based facilities such as storage tanks and pipelines are the third major source of oil pollution and are estimated to account for 40% of the oil-pollution incidents in this country. The Secretaries' Report states that:

> There is no readily available compilation of the number, size, and character of the facilities for moving and storing these materials [scil., oils and liquid chemicals]... Extensive coastal and riverside terminal facilities, now numbering about 6,000, have been developed for the transfer of commodities between water and land [but]... products arriving at or departing from these water-side facilities may be handled several times. Both crude and refined products may travel via pipeline, railroad or tank truck as well as by marine vessel, producing almost endless possibilities for the discharge of oil....This country is laced by an estimated 200,000 miles of pipelines operating at pressures up to 1,000 pounds per square inch. These lines carried more than one billion tons of oil and other hazardous substances in 1965. Many sections of this network are laid in and across navigable waterways and reservoir systems.... Thus, our pipeline transport system involves the risk of oil pollution in our watercourses, port areas, and critical drinking water supply areas.[15]

Pipelines also break under water. Capt. William A. Jenkins, Deputy Chief, Office of Operations, U.S. Coast Guard, has testified before Congress on the frequency of pipeline breaks in the Gulf of Mexico. The Coast Guard had received reports from pipeline breaks in the lower Mississippi Delta area and Louisiana Coast area around the Morgan City area.

Some of these breaks have occurred due to marine casualties or other unknown sources. They have been of varying sizes, some quite sizable, and have gone into the swampy bayou areas. Capt. Jenkins supplied the Committee with a list of six recent incidents of pipeline breakage.

CONCLUSION

The potential for oil pollution exists anywhere oil is handled or used. Though catastrophic oil discharges usually receive immediate Government and public attention, the smaller spills and discharges, particularly those that take place during oil transfer operations, often go undetected until the slick washes up on shore and someone complains. Because many oil discharges go unnoticed and unreported at the time they happen, a means to identify the oil discharges from these oil transfer operations would offer more control. The offender could be identified and official action taken to ensure that: (1) the cause(s) of the illegal discharge was corrected and (2) proper cleanup operation was undertaken by the offender to remove the pollutants.

Tagging systems could be of particular value in monitoring oil spills that can take place when oil is transferred from ship to barge, barge to storage facility, or storage facility to pipeline operations and indeed where any similar oil transfer operation is undertaken.

But several criteria must be met if an oil tagging system is to be useful. The system must be acceptable to producers, processors, shippers, consumers, enforcement agencies, and the courts. Further, if tagging materials are added to the oil they must be compatible with the oil and not affect its subsequent use. The tagging system must uniquely and legally identify those responsible for the oil spill and its consequence. Regulations will have to be developed to govern the handling of oil during shipment and transfer and the discharge and disposal of oil wastes near port and on the open seas. Although waterborne sources are estimated to account for more than half the pollution, land-based facilities account for 40%. Thus, any movement of oil — loading, unloading, storage, and transfer — constitutes a threat. Accidents, poor maintenance, carelessness, ignorance and willful neglect, and lack of concern for the environment contribute to the problem. Though the largest potential sources of catastrophic oil pollution are few in number and usually quickly identified, the thousands of unidentified spills that appear "mysteriously" on the water or on the beach must be prevented. The problem becomes that of identifying these less publicized sources of oil pollution cheaply and conclusively.

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SECTION II

CHANGES IN OIL SLICKS

2.1 General

When oil is spilled on water, three major variables affect the fate of the slick: (1) the composition of the oil; (2) the nature of the receiving body of water (whether fresh, salt, or brackish), its temperature, motion, microbial population, and chemical contents; and (3) such diverse environmental factors as insolation, latitude, wind, atmospheric contents, and the like.

Oil, of course, is no simple compound or mixture of compounds: Crude oils show enormous variation in chemical content, both quantitatively and qualitatively. The literature on this point is immense, but there is special merit in the reviews of Bestougeff[17] (hydrocarbons on crude oils) and of Costantinides & Arich[20] (non-hydrocarbons). Naturally, variations in chemical makeup are accompanied by variations in physical properties of the molecular mixture: specific gravity, water solubility, volatility, viscosity, melting point, etc. Perhaps the largest event in the history of an oil slick is the evaporation of the light fractions. While the rate of evaporation will be influenced by many variables (wind velocity and turbulence, temperature of air and water, rate of the slick's spread, wave action, etc.), after several days at sea the slick will consist almost entirely of compounds whose boiling point is above about 700° F,[18,21] viz, compounds containing at least 20 carbon atoms, and probably of complex chemical structure. (For example, while crude oils from Montgomery County, Texas, contain only a small residue above 600° F, oils from Louisiana's Plaquemines Parish are frequently almost half residue.[22] Blokker[19] has analyzed the spreading and evaporation of several kinds of oil slicks. He reports that spilled oil rapidly spreads to a film 2 cm thick; although many variables affect its subsequent thinning, its final thickness will be 10-100 microns on pure water, but approximately 1 mm on heavily contaminated water.

While evaporation undoubtedly accounts for most of the volumetric loss in the slick, Dean[21] has suggested that solution in sea water may also play a significant role. For while the lightest hydrocarbons have finite solubilities in water, some heavier petroleum constituents, while undoubtedly less soluble, may still go into solution, for we are considering huge volumes of sea water. Dean notes that if a solubility on the order of one part per million is assumed, the whole cargo of the Torrey Canyon could have been dissolved in a patch of sea 20 miles square and 500 feet deep. In this connection, the presence of surfactants in natural crudes (e.g., such surfactants as vanadyl porphyrins) assumes a new significance. Several compounds of these metals in petroleum are known to be soluble in water.

As the light fractions and some of the metallic compounds disappear from the slick, other processes act upon the residue. While many of the common constituents (such as paraffins) are rather inert, some readily participate in chemical reactions and others become reactive in the presence of: strong sunlight (especially the ultra-violet spectrum); reaction intermediates in the slick itself and in the surrounding sea; atmospheric oxygen and ozone; and miscellaneous sources of chemical and physical energy. The slick may also be attacked by many microbial species that are common in both fresh and salt water. These several processes are discussed at length in the following sections of this report (2.2-3.3), Many of these processes are affected by ambient temperatures, and all of them are undoubtedly affected by the slick's dispersion; the degradation of such stable emulsions as "chocolate mousse" is surely impeded by the small surface area offered to the open sea and sky.

2.2 The Chemistry of Weathering

2.2.1 Introduction

To control violations of water-pollution regulations a system for identifying violators must be devised and instituted. One approach is to identify the violator through analysis of the components (intrinsic or added) of the oil slick itself. Analytical technology and "fingerprinting" (i.e., analytical determination of characteristic chemical and physical properties of the oil) can be applied to petroleum analyses with a reasonable degree of sensitivity and precision. However, interpretation of the results obtained through analytical technology is difficult when the technology is applied to a continually changing system. These difficulties apply principally to assigning, on the basis of slick composition, unequivocal legal responsibility for an oil spill: One has to consider that the composition of the slick may not be identical to that of the unspilled oil. The changes in chemical composition the oil undergoes is a function of many factors, the absolute number of which depend on the site of the spill (for example, fresh or sea water), environmental conditions (continuous exposure to sunlight, microbial content of the waters), and the time interval between the occurrence of the oil spill and the analysis of the slick.

At present only a general knowledge exists regarding the changes that crude oils and other petroleum products undergo when exposed to various natural forces (i.e., weathering). We all acknowledge the fact that the oil changes its character because of oxidation, solar radiation, and microbial action, but information about the specific mechanisms and reaction products that result is sorely lacking. This information is absolutely essential so that a rational and cogent interpretation of the analytical results can be used to assign liability to the violators of pollution regulations.

2.2.2 Catalytic Oxidation of Petroleum

Oxidation is one of the primary processes in the weathering of petroleum. Oxidation by air at ordinary temperatures (10 to 40° C) is commonly referred to as autoxidation; hydrocarbons seem to be oxidized in a chain reaction that involves hydroperoxide radicals. The fundamental theories of Bakh[23] state that the primary oxidation products are peroxides. Emanuel'[24] and his coworkers[25] have shown that the low-temperature, liquid-phase oxidation of hydrocarbons proceeds through several peroxides and hydroperoxides. The following mechanisms have been postulated:

(1) $RH \longrightarrow R^\bullet + H$

(2) $R^\bullet + O_2 \longrightarrow RO_2^\bullet$

(3) $RO_2^\bullet + RH \longrightarrow ROOH + R^\bullet$, etc.

(4) $RO_2^\bullet + RO_2^\bullet \longrightarrow ROOR + O_2$

(5) $ROOH \longrightarrow RO^\bullet + {}^\bullet OH$

(6) $RO^\bullet + RH \longrightarrow ROH + R^\bullet$

(7) ${}^\bullet OH + RH \longrightarrow H_2O + R^\bullet$

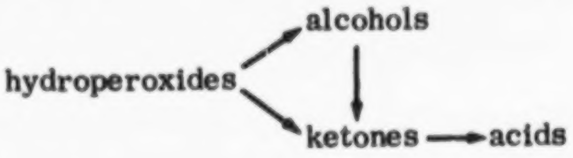
(8) $ROOH \longrightarrow RH \longrightarrow 2ROH$

(9) $ROOH \longrightarrow R_1COR_2 + H_2O$

(10) $ROH \longrightarrow R_1COR_2$

(11) $R_1COR_2 \longrightarrow$ acids

Reaction (1) starts the oxidation chain and feeds the cycle of reactions (2) and (3). The chain usually ends with reaction (4), in which $RO_2^\bullet$ radicals combine. The decomposition of hydroperoxide ROOH to give $RO^\bullet$ and ${}^\bullet OH$ radicals (reaction (5)) occurs relatively infrequently since rupture of the O-O peroxide bond requires 30 to 40 Kcal/mole. (It will be shown later that solar radiation can meet such energy requirements.) $RO^\bullet$ and ${}^\bullet OH$ yield $R^\bullet$, the basic radical for the oxidative chain, as a result of reactions (6) and (7). The breakdown of hydroperoxide according to reactions (8) and (9) leads to the production of alcohols and ketones, which are also obtained by the oxidation of alcohols according to reaction (10). Finally, acids are produced from ketones according to reaction (11). Integrating all of these steps, the following scheme emerges.[26]



Peroxides and hydroperoxides appear to be the primary products of the liquid-phase oxidation of unsaturated, alkyl-aromatic, and alicyclic hydrocarbons.

The kinetics of the oxidation depend on the oxygen partial pressure, and temperature, and the hydrocarbon; the total quantity of products formed is a complex function of the rate constant for the decomposition of peroxides.[25] The kinetic curve is S-shaped: After an initial induction period, there is a period of increasing rate followed by an asymptotic leveling off of the rate of oxidation and finally the reaction ceases. Tinyakova et al. (1965)[27] found that free radical production can occur at low temperatures (20-50° C) in both aqueous and hydrocarbon media in the presence of an oxidation-reduction system (reversible system) such as described by the general equation below:

$$ROOH + M^{n+} \longrightarrow RO^{\bullet} + M^{(n+1)+} + HO^{-}$$

The oxidation-reduction system can be provided by low concentrations ($\geq$0.002M) of metal salts. For example, H_2O_2 decomposes in the presence of ferric iron at 20° C; hydroperoxide can decompose at 50° C under the same conditions. We infer therefore that ferric iron in sea water (0.01%)[45] may increase the oxidation of petroleum hydrocarbons through free-radical mechanisms. (Of course, the situation is not simple because there are often oxidation-reduction inhibitors in the oil itself; sulfur compounds in petroleum are sometimes potent inhibitors, though these compounds, too, may be chemically altered in the slick.) In this connection, Gureyev and Soblina (1965)[25] found that different hydrocarbon fractions had different sensitivities to oxidation by free radicals. The kerosene fraction was more sensitive to the oxidative action of metals (Cu, Fe) than the gasoline (benzene) fraction.

The amount of atmospheric oxygen which diffuses from the surface into the bulk of the liquid affects the reaction. Since the concentration of the oxygen penetrating into the oil is generally low and the temperature is relatively low, the oxidation is slow.[28] However, some oxidation occurs rather rapidly. The experience of Arozena[28] is instructive.

> A crude petroleum of Syrian origin and a commercial hydrocarbon, gas-oil, were used. The petroleum was not used directly because, when it is put in contact with water (whether sweet or salt), its tarry [asphaltenic] components agglutinate and form small spherical masses; meanwhile, the oily matter spreads out on the surface of the water, forming a uniform film without [any phase of] continuous solution . . . . For this reason we thought it important to eliminate the semisolid phase of tars and asphaltenes . . . . [The crude oil was distilled at 300° C, the middle distillate reserved, and the residue rejected.]
>
> We must report that these fractions, [even] after distillation, were not refined; they therefore contain sulfur and substances that can unite with oxygen to form resins. We analytically verified the presence of sulfur [in distilled fractions] and observed in the distillate, above all when it was hot, the formation of new tarry materials upon passage of air through these fractions. In this last-mentioned case, however, [the tars] do not agglutinate as in the crude and, therefore, do not create problems of discontinuity in the [oil] films; furthermore, the quantity [of tars] is so

> small that they remain dissolved in the light and middle fractions of the petroleum when these fractions are put in contact with water.
>
> The composition of the petroleum must be kept in mind when studying the passage of oxygen through oil slicks of distinct thickness. According to the petroleum's chemical composition, the thickness of the oil film being held constant, a petroleum will fix more or less oxygen. In our case, we used only one type of petroleum, whose composition remained constant. . . .
>
> --JH, trans.

In addition to peroxides, free-radical production can also be initiated by the presence of acidic gums (non-distillable resins) and "oxyacids" which are the result of secondary processes (reaction 11).[28]

2.2.3 Photochemical Oxidation

In spite of the absorption of the shorter wavelengths of the sun's rays by the atmosphere—which reduces the ultraviolet (UV) light of less than 4000 Å to no more than 5% of the total[29]—there remains enough energy in the residual radiation to break a variety of chemical bonds.

Table 1 illustrates several of the many possible primary photochemical processes which occur on the excitation of polyatomic molecules.[30] The polyatomic molecule ABC, in the singlet (S_1) or triplet (T_1) states, can undergo modification by a variety of photochemical processes. Obviously, all these processes are not relevant to the breakdown of water-borne petroleum. Reactions (1), (2), and (6) may be the principal photoreactive processes responsible for the observed changes in petroleum exposed to weathering.

In fact, according to Ellis and Wells,[31] enough energy is provided by the shorter wavelength solar radiation (2100 to 3100 Å) to conclude that several of the foregoing reactions may serve as the primary initiator of autoxidation of petroleum. Figure 1 shows the relationship of the energy content of visible light and UV radiation to its wavelength. It can be seen that the energy needed to break a number of bonds can be provided by solar radiation at the earth's surface.

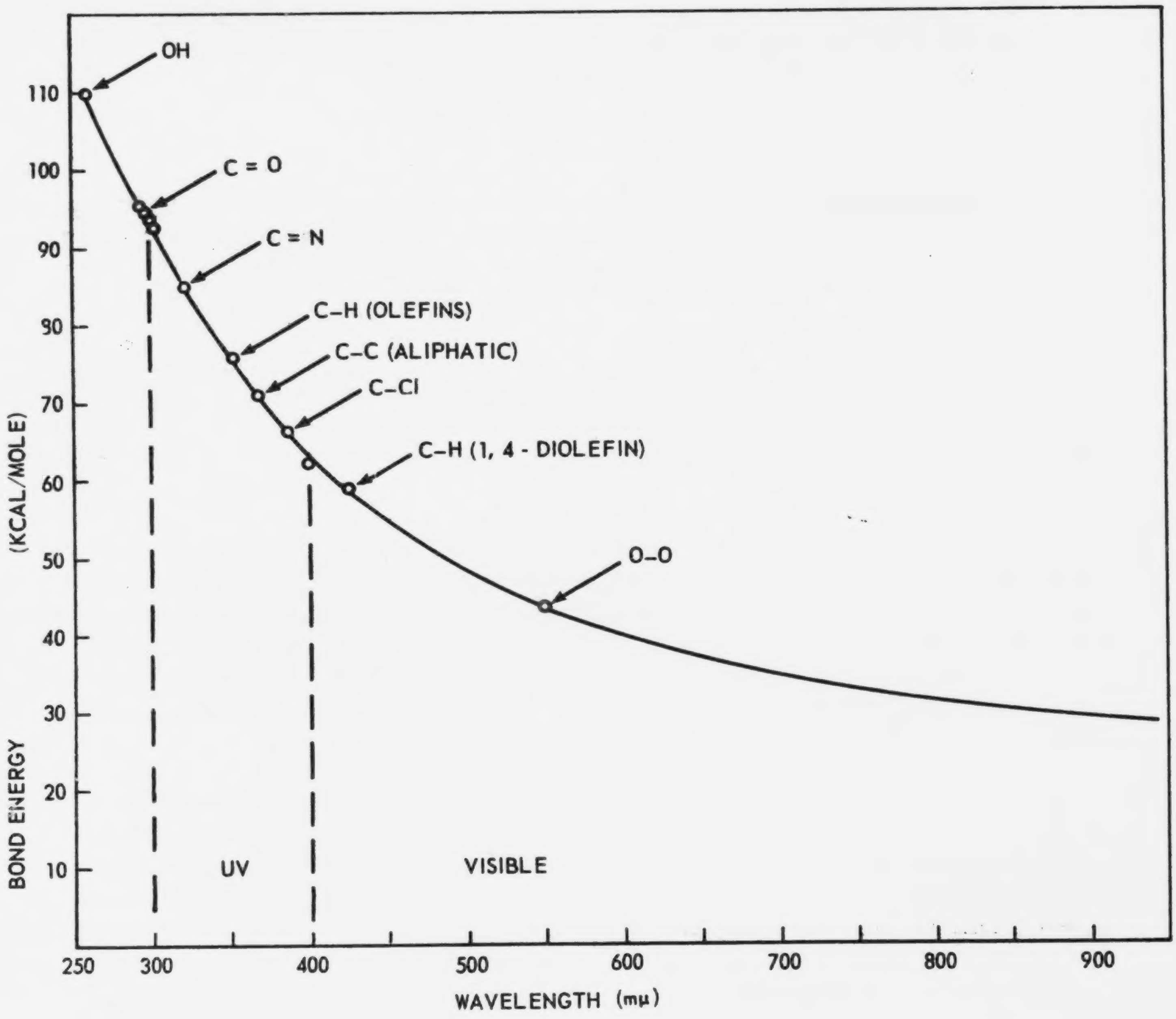


Figure 1. Bond-Dissociation Energies and Double-Bond Activation Energies for Chemical Groupings Present in Some Autoxidizing Media (Reproduced from Scott)

TABLE 1[30]

PRIMARY PHOTOCHEMICAL PROCESSES

$ABC(S_1)$ or $ABC(T_1)$	$\rightarrow AB + C$	Dissociation into radicals	(1)
	$\rightarrow E + F$	Intramolecular decomposition into molecules	(2)
	$\rightarrow ABC$	Intramolecular rearrangement	(3)
	$\rightarrow ABC^1(S_1)$ or $ABC(T_1) \longrightarrow ABC^1(S)$	Photoisomerization	(4)
	$\xrightarrow{RH} (ABCH) + R$	Hydrogen-atom abstraction	(5)
	$\xrightarrow{ABC} (ABC)_2$	Photodimerization (photoaddition)	(6)
	$\rightarrow ABC^+ + C^-$	Photoionization	(7)
	$\xrightarrow{D} ABC + \text{Products}$		
	$\rightarrow ABC^{+(or-)} + D^{-(or+)}$	"External" electron transfer	(8)
	$\rightarrow AB^+ + C^-$	"Internal" electron transfer	(9)

For the various general components to be found in petroleum, photochemical modification (at 2500 to 3300 Å) can occur by the mechanisms shown in the following series of equations:

Aldehydes: $RCHO + h\nu \longrightarrow R + HCO$, R = alkyl or aryl

Ketones: $CH_3COC_2H_5 + h\nu \longrightarrow CH_3CO + C_2H_5$

$\longrightarrow CH_3 + COC_2H_5$

Organic Acids: $RCOOH + h\nu \longrightarrow R + COOH$ (or $CO_2 + H$)

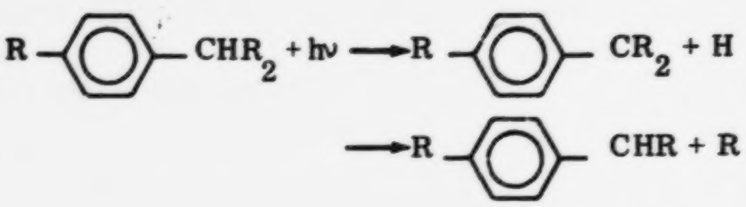
$\longrightarrow RCO_2$ (or $R + CO_2$) $+ H$

$\longrightarrow RCO$ (or $R + CO$) $+ OH$

$\longrightarrow RH + CO_2$

Paraffinic Hydrocarbons: $RCH_2R + h\nu \longrightarrow RCR + H_2$ (1470 Å)

Aromatic Hydrocarbons:



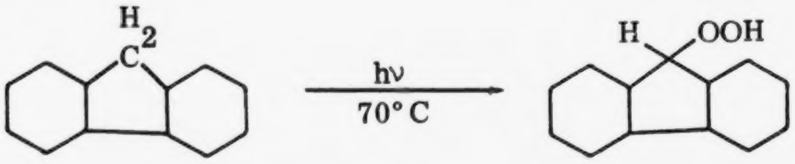
It can be seen that a number of radicals can be formed from petroleum constituents (aldehydes, ketones, acids) by photochemical dissociation. These radicals then can serve as initiators of the autoxidation process. The reaction mechanism shown for the paraffinic hydrocarbons, however, will be infrequent under ambient conditions since it occurs primarily at 1470 Å. The aromatic hydrocarbons, in general, exhibit a greater stability to UV and visible radiation than the paraffinic hydrocarbons, even though they absorb strongly in these regions. Aside from the protection afforded by the conjugated ring system, this may be due to the fact that photo-decomposition modes of the aromatic molecules occur only with low quantum efficiencies in the first absorption bands (ϕ = 0.0001 or less).[30] In those compounds having alkyl groups attached to an aromatic ring system, exposure to light in the first absorption band may lead to rupture of the alkyl H-C or C-C bonds to form the benzyl-type radical.[32] All of the above mechanisms and the degree to which they are operative are affected by temperature, light intensity (determined by weather conditions, season, and geographic latitude), wavelength of the incident radiation, and concentration of reactants. Ellis & Wells[31] report that

> The color properties of petroleum may be destroyed by solar UV rays. Petroleum oils intended for use as lubricants and which may have gumming properties due to unsaturated components are improved in quality by exposure to UV radiation in an inert gas. Apparently polymerization occurs, resulting in the formation of saturated bodies.

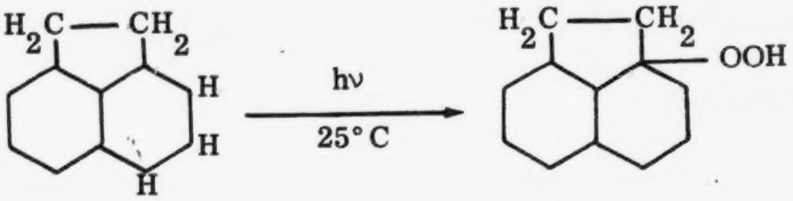
The addition of sulfur (0.01 to 0.1%) was also deleterious, whether in the presence or absence of oxygen. In the presence of air or oxygen, it caused a marked increase in the amounts of color and gum formed. Acid formation and peroxide number were also greater than in the absence of sulfur. It also appears "that sunlight lowers the induction period for gum formation but water has the opposite effect" with stored samples of petroleum. In addition the rate of gum formation was observed to triple for approximately every 20° F rise in temperature.

Tipson[33] has reviewed the various mechanisms of polycyclic hydrocarbon degradation by oxygen and UV at low temperatures (< 100° C). Some of those reactions which are typical of the autoxidation mechanisms applicable to crude petroleum are as follows:

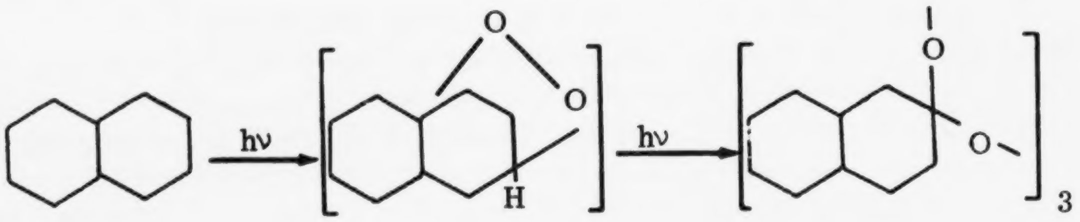
On treatment with O_2 and UV light for 30 hours at 70° C, fluorene in benzene gives the stable 9-fluorenyl hydroperoxide:



Treatment of 2a, 3, 4, 5-tetrahydroacenaphthene [sic] with O_2 and light for 150 hours at room temperature gives the hydroperoxide:

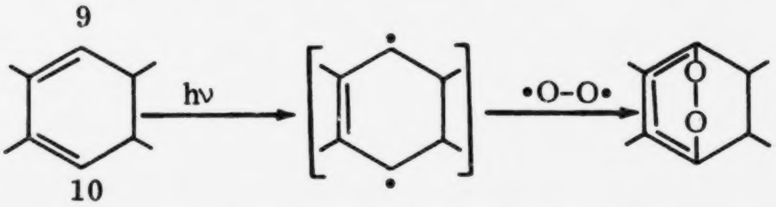


1, 2-dihydronaphthalene at 18° C for 430 hours gives the unstable para-transannular peroxide with O_2, which rearranges to a trimer.



Solutions of anthracene stored in the open air for long periods of time form the insoluble anthroquinone. Molecular oxygen can also be added across the central ring to give the 9, 10 peroxide. Naphthacene and pentacene are photo-oxidized more readily, and the reactions occur so readily with hexacene and heptacene that solutions of these hydrocarbons, exposed to air and light, are almost instantaneously photo-oxidized. The nonlinear hydrocarbons react with oxygen less readily than the linear polyacenes, or not at all.[33]

Under the action of UV light, transannular addition of oxygen occurs at the most reactive centers of linear aromatic hydrocarbons if the two reactive centers are para to each other (as in the anthracenoid hydrocarbons) giving transannular peroxides.

> It seems probable that under these conditions the absorbed light excites the dienoid structure to a diradical which then rapidly reacts with the oxygen diradical. The overall process involves consumption of the diradicals with no regeneration; hence these are not chain reactions. The transannular
>
> 
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> reaction of oxygen is further facilitated by the presence of electron-donating substituents (e.g., methyl or phenyl) at the reactive centers.[33]

2.2.4 Metalloporphyrins

Another important component of crude petroleums is the metalloporphyrins. Although the porphyrins found in petroleum are stable to heat and to concentrated acids,[34, 35, 36] porphyrins, as a category, are relatively unstable to light, peroxides, and to various forms of ionizing radiation[37, 38] (X-, β- and γ-irradiation). In most of these cases, the nucleus is unaffected; however, in the case of oxidation initiated by photochemically generated hydroperoxides, the side chain may be modified so that the porphyrin can become water soluble.[37] In view of the fact that petroporphyrins and their complexes, being large, planar aromatic molecules, can act as surface-active agents, they would tend to concentrate at oil water interfaces,[34, 35, 38, 39, 40, 41] thereby increasing the probability of cation exchange and oxidative degradation. Such processes (conferring a change in the partition coefficient of the porphyrin) would result in an alteration with time on the order of weeks of the final metalloporphyrin content of the petroleum. The extent of the partition of porphyrin between the oil slick (organic phase) and the water depends on the hydrophobic nature of the ring and the hydrophilic nature of the central nitrogens and the polar side chains.[42]

In an interesting publication by Wolsky & Chapman,[43] in which the authors describe their attempts to isolate and identify vanadium and nickel porphyrin aggregates from Boscan asphaltines by the Groennings' method,[44] a few oxidation studies were performed to check the stability of the porphyrin aggregate. The results showed that oxygen alone had little effect but, together with UV light, caused rapid decomposition of the porphyrins. Although the authors do not describe the details of their oxidation study, nor do they give any indication as to the identity of the decomposition products, it is of more than passing interest that UV radiation demonstrated so pronounced an effect on the putatively stable porphyrins.

The preceding discussion points out the physicochemical lability of several of the natural constituents (aliphatic, aromatic, porphyrin) of crude petroleum. These facts demonstrate the potential difficulties one is faced with in attempting to identify unequivocally a specific crude oil solely by virtue of the concentrations of its intrinsic components, especially with a sample that has undergone prolonged exposure to many indefinable and uncontrollable environmental and climatic conditions.

2.3 Microbial Oxidation

Biochemical degradation of oil slicks is a natural consequence of oil spilled on anything but distilled water in a sterile inert atmosphere: Both fresh and salt water normally contain a diverse microfloral population, and many microorganisms of aquatic habitat are known to metabolize petroleum compounds, especially hydrocarbons, via oxidative pathways. Only one other generalization should be risked: Even under optimal conditions for microbial growth, the heavy, complex molecules characteristic of aged oil slicks are not rapidly metabolized to either stable cellular components or to oxidative end-products; however, it should be borne in mind that while disappearance of the slick is one thing, its biochemical alteration is quite another matter. If due respect is paid to the scope and complexity of oil-pollution environments, to the diverse species distribution of microflora in open water, to the variations in metabolic competence within even such well-known hydrocarbon-utilizing species as Pseudomonas aeruginosa, to the chemical diversity of crude oil, and to the numerous reactions that may in time alter the molecular makeup of the slick, the whole question of microbial oxidation must be approached with extreme circumspection.

According to a most authoritative treatise on marine microbiology,[46] there are approximately 700 species of marine microflora. Bergey's Manual of Determinative Bacteriology,[47] the standard American reference, recognizes 183 bacterial species of marine origin; ZoBell & Upham[48] list 165 species that are not recognized in Bergey; and Brisou[49] lists 57 more species that are not listed in either Bergey or in ZoBell & Upham. However, as Kriss[46] himself points out: "Because of overlaps and technical obscurities in the art of microbial systematics, we should not conclude that Bergey's list should be doubled." Nevertheless, he suggests that 700 is perhaps a more realistic number. Kriss may be wrong, but it would be hazardous to argue the point because he has conducted an immense field survey of marine microflora at all depths and at a great number of locations in the Black Sea, the Greenland Sea, the Norwegian Sea, the central Arctic Ocean, the Atlantic Ocean, the Indian Ocean, and the Pacific Ocean. He has also investigated the biochemical activity of more than 3,000 strains of marine microfloral heterotrophs. Although he did not use hydrocarbons as growth substrates, his findings have great significance because they do reveal the extraordinary metabolic variations in marine microorganisms as a function of latitude; moreover, these variations are likely to be paralleled in the ability to utilize hydrocarbons. His findings are of the first importance, and should be quoted at length:

> A world-wide geographical distribution pattern of microbial forms occurring in the sea and using readily assimilable organic matter in their vital processes clearly emerges [from our world-wide study]. The polar regions -- Arctic, Antarctic, sub-Arctic and sub-Antarctic -- are areas of very low saprophytic bacteria population density. Although the productivity of the ocean water is conditioned by a rich plant life, the metabolic products and dead remains of the organisms inhabiting these parts of the ocean do not create such a concentration of nutrient material for saprophytic microorganisms as is observed in the equatorial-tropical regions of the ocean.

That this is so can be seen from the high concentration of microbial life (saprophytic bacteria) in the equatorial and tropical zones of the Pacific, Indian and Atlantic Oceans. These zones are in marked contrast to other geographical zones of the world's seas and oceans in respect to their microbial wealth. It is interesting that a high concentration of bacteria assimilating labile organic matter is observed in those geographical regions of the ocean which are poorest in plant and animal life by comparison with the high latitudes. [p. 274]

It is a striking fact that the equatorial-tropical zone is distinguished by the low concentration of biochemically active microbial forms among the saprophytes inhabiting it. In the Arctic, sub-Arctic, Antarctic and sub-Antarctic regions of the ocean the percentage of bacterial strains causing thorough breakdown of proteins proved to be four to sixty times greater, and the percentage of those fermenting carbohydrates two to eleven times greater, than in the equatorial zone.

These data suggest that the process of organic decay and liberation of nutrient elements is more vigorous in high latitudes. Although the saprophyte population there is not so great as near the Equator and the biochemical activity of the saprophytes is affected by the low temperatures, nevertheless, the presence of a comparatively large number of microbial forms possessing diversified enzymatic activity makes for more thorough conversion of organic matter in the high latitudes than in the tropics. [Emphasis supplied.]

The result is that in the Arctic, sub-Arctic, Antarctic and sub-Antarctic regions the sea water contains a higher concentration of the nutrient substances essential for the development of aquatic vegetation.... [pp. 276-277].

The reasons for the poverty of tropical water in biochemically active microbial forms and for the higher concentration of these forms in high-latitude water are still unknown. The relatively high concentration of allochthonous organic material readily assimilable by microbes in tropical waters, which accounts for the high density of the saprophytic population in the equatorial-tropical zone, may, perhaps, obviate the necessity for enzymatic reactions ensuring total utilization of the organic material. In high-latitude water the scanty food supply leads to the elaboration of adaptations in the saprophytic bacteria, enabling them to make more economic use of the organic matter by taking advantage of its more thorough decomposition and conversion. [p. 277]

In short, cold waters are much more likely to contain petroleum-metabolizing bacteria than warm waters. There is every reason to think that the microbial attack on the Ocean Eagle's slick (in Puerto Rico) was drastically different from the Torrey Canyon's (in the English Channel).

Long lists of microorganisms capable of metabolizing petroleum have been published by Beerstecher[50] and by Davis.[51] We find, however, that the work of McKenna & Kallio[52] and of Van der Linden & Thijsse[53] is much more rigorous and reliable; these authors are also the best guides to the literature. It is well to begin this discussion with McKenna's warning:

> Codification of the numerous microbial forms capable of degrading or assimilating hydrocarbons has not been attempted on several grounds. Many reports carry descriptions of new isolates that are, to be kind, meager. Bacteria, yeasts, and fungi possessing the capability are legion, new members of this group are continually being found, and such a list would be relegated to senecide [sic] before it appeared in these pages. Fühs prepared a list of organisms capable of growth at the expense of hydrocarbons -- it comprises over 100 yeasts, bacteria, fungi, and actinomycetes. It is clear that if attention is paid to detail and if a modicum of experimental imagination is indulged in, a wide variety of microorganisms, not originally selected for the character, can be shown to be hydrocarbon-utilizing organisms. Appropriately selected and cultivated organisms grow at the expense of diverse hydrocarbons as well as, or better than, on the common substrates widely used in microbiology. Under a variety of conditions oxidation products appear in culture fluids and can be subjected to chemical analysis; such chemical identification has permitted meaningful formulation of microbial hydrocarbon degradation pathways.[52]

Although there are hundreds of articles on hydrocarbon microbiology (Van der Linden & Thijsse[53] listed 285 of the most important in 1965), most of them deal with molecules having less than 20 carbon atoms; all the rigorous scientific literature is suggestive but not relevant. While not every species has been able to metabolize every n-alkane in every experiment, Van der Linden & Thijsse had no difficulty finding at least one microbe that had been reported to attack each n-alkane at least some of the time. Isoparaffins have been less studied, but they too (at least the lighter ones) are metabolized (often in several ways) by several common bacteria of marine habitat. Van der Linden & Thijsse suggest that olefins may be more readily oxidized than alkanes, and advance several cogent reasons in support of their argument. Although there have been very few studies of cycloparaffins (naphthenes), they seem resistant to most microbial attack:

> Cycloparaffins seem to be poorly utilizable by microorganisms in general, and, in consequence, bacteria that would enable the study of their biodegradation pathways have only been encountered twice.... [In one of these studies, however,] no experimental details are given and no analytical methods are mentioned. This study, therefore, cannot be critically examined.[53]

The situation is not much better for aromatic and alkyl-aromatic compounds: Little is known for certain, and very little indeed is known about the rather heavy and complex molecules that are likely to be found in oil slicks that are several days old.

The situation is further complicated by the molecular diversity of crude oils. While most studies of microbial hydrocarbon metabolism have tested only one hydrocarbon at a time, there is strong evidence that (paradoxically) two different hydrocarbons may be more readily oxidized together than separately:

> Hydrocarbons seemingly resistant to both oxidation and assimilation may be oxidized if attacked by organisms concomitantly oxidizing other, utilizable hydrocarbons. Co-oxidation... may be a widely occurring phenomenon in microbial metabolism.... The extraordinarily high yields of co-oxidation reactions are prime targets for technological developments in commercial hydrocarbon conversion by microbial reactions, but no such studies have been published.
>
> Another phenomenon noted during investigations of bacterial hydrocarbon degradations in oxidation of a substrate (commonly but not invariably a hydrocarbon), followed by metabolite accumulation in the face of an apparent inability of the relevant organism to assimilate the oxidation product -- materials so oxidized are somewhat inelegantly referred to as "nongrowth" substrates.... Like co-oxidation, oxidation of nonassimilable substrates may be a widespread phenomenon in the microbial kingdom; together with co-oxidation, the process complicates studies of hydrocarbon metabolism based on assimilation studies, and raises intriguing questions of substrate specificity to say nothing of the assimilatory complex in bacteria.[52]

The process of microbial oxidation of oil slicks, known to be rather slow at sea, also seems to be slow in the laboratory. It has recently been shown that oil slick collected at sea but cultivated in the laboratory is barely assimilated after several weeks of microbial growth.

Because of the various ways that aquatic bacteria can alter oil slicks, chemical tracing of slicks to suspected sources may be difficult to prove in court. This proposition is *a fortiori* true when added to the evidence for straight chemical changes in oil slicks (section 2.2 of this report).

SECTION III

PASSIVE TAGGING

3.1 General

Passive tagging is a convenient circumlocution for no tagging at all: Nothing is added to the oil, but the slick sample is subjected to various methods of physical and chemical analysis. The sample itself must provide all the evidence for detection and identification. By an obvious extension of a figure of speech, passive tagging is sometimes called physico-chemical "fingerprinting." Petroleum geochemists have devoted considerable effort to documenting chemical differences among crude oils, and anyone who cares to take the trouble will have no difficulty finding major differences between most Tertiary crudes and most Paleozoic crudes. However, the problem of legally identifying oil slicks (i. e., of proving liability for oil pollution in a court of law) has more to do with a branch of criminology, which, for want of a better phrase, we might call "forensic chemistry," than with geochemistry, analytical chemistry, or petroleum chemistry. For the central problem in this application of forensic chemistry is: Can this sample of slick be proved irrefutably to have come from a tanker known to have been in the area, or from a pipeline nearby, or from a storage tank, or what have you?

The most direct method of proof (and the only one that we have seen suggested) is to compare the slick with the unspilled cargo (or fuel) of the suspected source of pollution. However, as we have already seen in section 2, unless the slick is very fresh, we have every reason to believe that it will differ from the suspect cargo: The slick will have been irradiated, mixed with complicated aqueous solutions (sea water, polluted fresh water, or brackish swamp water), exposed to oxygen and air pollutants, and intimately associated with a variety of aquatic microbes; depending on local conditions, it will have been partially evaporated, emulsified, and photolyzed, and may have undergone autoxidation, photopolymerization, enzymatic oxidation, and ionic exchange.

What part of the fingerprint can be stable to all these conditions? Heavy and highly branched alkanes are excellent candidates; so are the heavy and complex hydrocarbons of mixed structure that are common in lubricating oil. However, the heavy branched alkanes are (in general) exceedingly rare in oil.[54] Bestougeff,[55] for example, has pointed out that:

> The distrubtion of branched-chain paraffins in different fractions of a crude oil is unequal, and, as in the case of n-paraffins (light crude oils), drops rapidly as a function of the molecular weight.

The very complex hydrocarbons that are characteristic of lubricating oils are even more difficult to identify precisely: Whitehead & Breger[56] do not mince their words:

> The compounds thus far isolated from crude oil are rather simple and include basic paraffinic, cycloparaffinic, and aromatic types. A few more complicated multiple-ring structures, such as adamantane and some bicyclooctanes, have also been identified, but the complex structures of the lubricating oil fraction can only be described in very general terms. Here, where the compounds may be composed of mixed aromatic, cycloparaffinic, and paraffinic structures, the number of possible compounds becomes almost infinitely large and the likelihood of positive identification of any one becomes vanishingly small.

Even though several hundred compounds have been identified in crude oil, the identified compounds "probably account for well under 50% of the constituents of a crude petroleum."[56] It should be apparent that the hydrocarbons in slicks of crude and heavy oils will contain an even higher percentage of unidentified structures. One must therefore conclude that although heavy, complex hydrocarbons are likely to be stable constituents of oil slicks, they will not serve as passive tags because they are exceedingly rare, exceedingly difficult to identify, or both.

What other stable constituents might be used to fingerprint oil? Trace metals (especially vanadium and nickel) and isotopic ratios have been suggested, and these will be examined in detail in the next two sections. These two approaches to passive tagging have been chosen for special study for more than their analytical attractiveness: Each in its way illustrates the difference between forensic chemistry and analytical chemistry.

In general, the requirements on passive tags should not be different from the requirements on active tags. Both kinds of tags should be unchanged by weathering and microbial action, soluble or dispersible in oil, insoluble and nondispersible in water, and involatile. However, there are special circumstances in which some of the requirements on passive tags may be relaxed. Where oil pollution is infrequent, where there are few possible sources of pollution, and where weathering may be assumed insignificant or inconsequential (because of the slick's freshness), several methods of chemical analysis—supplemented by a great deal of convincing circumstantial evidence of an extra-chemical kind—may identify oil slicks by passive tags in the spilled oil. Some characteristic methods of this sort are discussed in section 3.4. The reader is reminded that these methods are valuable only where the circumstantial evidence is already convincing; they must be considered as presumptive, not confirmatory, tests.

3.2 Metals

Many inorganics have been found in petroleum ash: Ag, Al, As, B, Ba, Ca, Ce, Co, Cr, Cu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pt, Ra, Rb, Rn, Si, Sn, Sr, Te, Ti, Tl, V, U, Zr, and Zn. The literature on trace elements in crude oils has been the subject of several very important reviews.[57] Many of the elements listed above are not frequently found; others are frequently found in low concentrations; only a few, however, are frequently found in petroleum ash in concentrations above 0.1%, and of these few, special importance attaches to Ni and V.

These two metals are important because of the problems they cause industry:

> The volatility of certain metallic compounds may lead to their presence in distillate fractions, their concentrations increasing with the depth of the cut. Some of these alter the selectivity of cracking catalysts, increasing the formation of coke and hydrogen and decreasing the yield of gasoline. The more common metals of this type are nickel, copper, vanadium, and iron. Non-volatile vanadium, which concentrates in the residuum from which heavy fuel oil is produced, is extremely corrosive to refractories used in furnaces. Its most serious destructive effect is upon fire-clay bricks. Vanadium oxides form low melting eutectics with clay, producing hard, glassy slags which are extremely difficult to remove.[58] [pp. 4-6]
>
> Nickel is probably present to some extent in all crude oils, much of it in a volatile form. As an active dehydrogenation catalyst it alters the selectivity of cracking catalysts, and accurate determination of it in distillate feed stocks is therefore of importance.[58] [p. 179, emphasis supplied.]
>
> ... Vanadium is present in crude oils combined in porphyrins, some of which have low enough boiling points to permit the element to distill. Thus, it is found in gas oil cuts used as feed stock for catalytic cracking. In common with other elements of the first transition series, vanadium is a dehydrogenation catalyst with an activity from one-tenth to one-fourth that of nickel.[58] [p. 235]

Their presence also has geochemical significance, though authors of reviews (all of them magnificently qualified) often disagree on how much, if any. Based on work of Vinogradov and of Radchenko & Sheshina,[59] Manskaya & Drozdova[60] have concluded that

> Sulphur-poor petroleums contain significantly less porphyrin than sulphur-rich petroleums. In the former case, the porphyrins occur as nickel complexes, in the latter as vanadium complexes. [p. 145]

Dunning[61] has savagely attacked these conclusions:

> These conclusions seem illogical from the philosophical approach and doubtful even if the data are accepted as being generally applicable .... [They] illustrate the danger of drawing generalizations from data involving incomplete studies or too few oils. [pp. 398-399]

In a more recent review, however, Hodgson et al.[62] explicitly support the Russian conclusions:

> Radchenko and Sheshina have drawn attention to the relationship which exists between vanadyl porphyrins and sulfur in crude oils .... Evidence has been produced by Park and Dunning ... to discount the possibility ..., but the fact remains that there is some relation between sulfur in crude oil and the vanadyl porphyrin content .... It is well known that sulfur and vanadium compounds are very important factors in redox systems—possibly this could account for the simultaneous entry of the two substances into crude oil. [p. 247]

Vanadium and nickel in oil are also of interest to students of water pollution because they have been seriously proposed as valuable means of identifying the origin of oil spills. Canevari[63] has put the matter most directly:

> The method [we propose] simply entails measuring the vanadium and nickel contents of the unknown oil pollutant. There is a very specific amount of these metals associated with every crude—in essence constituting an individual metallic trait. There are other chemical and physical properties for the various crudes, but these are subject to change during weathering/aging [sic]. The metallic components, however, are stable and are not affected by weathering. By simply comparing the metallic content of the oil spill against [sic] that of the suspected source, it is possible to limit the probable source to a specific vessel, pipeline or storage facility. The technical feasibility of the metallic fingerprinting [sic] was demonstrated by Dr. George Milliman and Dr. David McMahon in a systematic analyses [sic] of actual oil spill samples as well as control samples.

Guinn & Bellanca[64] have argued a similar but more complex case for vanadium, sodium, manganese, and cobalt; they have concluded that their method

> ... offers definite promise for the trace-element characterization matching [sic] of an actual oil-slick sample with one sample of fuel oil—out of a number of suspect samples. The broader and deeper study now being initiated should establish this possibility more rigorously, and provide a mathematical basis for the interpretation of results obtained on oil and oil-slick samples obtained by enforcement

> agencies in the investigation of individual violations of oil pollution laws. The various characterizing trace elements, occurring in the original crude oils largely as essentially non-volatile metal porphyrins, remain in the residue left when the volatile components of the crude evaporate (as from an oil slick), and when the light ends are distilled off in refining. Thus NAA [neutron activation analysis] matching of the levels of these trace elements—between an oil slick and its polluting source—may, for the first time, provide a method of identification of the source of oil pollution of waters that will aid in the enforcement of present oil pollution laws.

The notion that trace metals, especially vanadium and nickel, might be suitable passive tags is by no means new. In 1955, Johannesson[65] reported that he had successfully used vanadium and nickel to identify oil slicks in Wellington, New Zealand, and had used this evidence to prosecute offenders. Because Johannesson's work has not been cited by current proponents of trace-metal tags (e.g., Canevari[63] and Guinn & Bellanca[64]), we quote a section of Johannesson's article here so that the reader may see how little the argument has changed over the years (although the analytical methods for determining trace-metal content have, of course, changed with the times):

> I have successfully used ... [a] method depending on the nickel and vanadium contents of the oils. The amounts of these elements present in oils varies [sic] considerably, as shown ... by Shirley [in a 1931 paper] ....
>
> Vanadium and nickel are held in the oils as co-ordinated complexes with porphyrins, and are not affected by contact with sea water; and, further, the concentrations of these elements in sea water are insignificantly small compared with those in the oils.
>
> Samples weighing 3 to 5 g are sufficient for analysis.... Ashing was carried out in a platinum basin, ethanol being added to facilitate removal of the water and the burner flame being directed, initially, on the surface of the liquid. [The reader must be warned that this method (direct wet ashing) has been severely criticized by all current authorities[57, 58, 66] on the inorganic analysis of petroleum because volatile constituents, especially organometallics, are very likely to evaporate; vanadium and nickel porphyrins are especially emphasized as compounds likely to be lost by direct ashing. McCoy[58] has pointed out that even in heavy residual oils, nickel porphyrins are evidently largely lost by direct ashing; see p. 184 of McCoy's excellent text.] A number of methods for the determination of vanadium and nickel in oils has been published and any of these may be used....

TYPICAL RESULTS

Source of oil	Vanadium pentoxide, mg per 100 g of oil	Nickel oxide, mg per 100 mg of oil	Ratio of vanadium pentoxide to nickel oxide
Recovered from harbor	14.0	13.9	1.01
From suspect source	12.0	10.2	1.17
A distillate fuel oil	trace	trace	---
Abadan	6.8	1.2	5.65
Curaçao	40.0	5.1	7.85
San Pedro	11.0	10.7	1.03

> These results established that the recovered oil was the same as that from the suspected source, allowance being made for evaporation and, further, that they were of San Pedro [Los Angeles County] origin.
>
> Liability was later admitted by the offending party and so the origin of the oils was confirmed.

The claims made in these proposals rest on several assumptions that are presented as fact. The central assumptions are: (1) The metallic content (especially vanadium and nickel) of crude and fuel oil is not affected by weathering; (2) the metallic content (more precisely, the ratio of metal to metal—because the metallic content increases as the slick evaporates) of the slick bears a known or fixed relation to the corresponding content of the unspilled oil; (3) these trace elements exist in oil as "essentially non-volatile metal porphyrins" that are chemically and physically stable in the slick. The facts, however, seem to be rather different from the claims.

Neither vanadium nor nickel is present in petroleum as a single molecular species; there are a variety of molecules containing these metals in petroleum, and not all of these molecules are either stable to oxidation or insoluble in water. Costantinides & Arich[66] have reviewed the evidence:

> Occasionally, traces of metals are found in the gas-oil fractions. Metal contents increase regularly with increasing molecular weight of the

> distillate fractions and reaches [sic] its maximum in the residue.... The occurrence of metals in distillates may be explained by a mechanical entrainment of residue or by distillation of the metals in the form of volatile metal-organic compounds. The latter view is generally accepted as a result of investigations...indicating that some metal complexes, isolated by elution chromatography and by extraction with aqueous pyridine, are concentrated in the more volatile distillate fractions.... These findings lead to the conclusions that both vanadium and nickel compounds of widely varying molecular weights exist in crude oils. [pp. 164-165]

Dunning has made enormous contributions to our understanding of metals in petroleum. He has also made it abundantly clear that many of these metals (especially nickel) exist in petroleum as water-soluble compounds:[61]

> Work of Erdman and associates (1956) and Dunning (1953) showed that [petroleum] porphyrins and their complexes generally are interfacially active. As a result, they might be expected to be concentrated at interfaces, and Dunning and associates (1954) used the water spray method...in an attempt to concentrate the porphyrin-metal complexes of North Belridge oil.... The large excesses of metals and nitrogen over that accounted for by the metal-porphyrin complex contents of these extracts points [sic] to the postulate that other metal-nitrogenous substances may be present.... The nickel and vanadium contents were increased more than the porphyrin or nitrogen contents in the pentane-insoluble portion of the water-spray extract. Apparently part of these metals in crude oil was not complexed with large nitrogenous molecules. This is in agreement with Garner and associates (1953). The rather high (0.01 weight %) nickel concentration in the water-soluble extract provides further evidence that the crude oil contained uncomplexed nickel. The nitrogen, nickel and vanadium contents of these water-spray extracts vary in the same manner as do the porphyrin contents. The ratios of porphyrin contents to the total nickel and vanadium contents are 3.0, 4.6, 4.1, and 6.8 in the propane-insoluble extract, whole crude oil, extracted crude oil, and propane-soluble extract, respectively. As mentioned above, the ratio of porphyrin to vanadium or nickel in a porphyrin complex is about 10:1. Thus, insufficient porphyrin was isolated in any of these fractions to complex all of the nickel and vanadium present. Extensive chromatographic and solvent-extraction procedures may produce petroleum extracts which contain vanadium primarily in the form of the vanadium-porphyrin complex. This observation has lead to some misinterpretations in the literature. It should be emphasized that such extracts, containing vanadium primarily as the porphyrin complex, are rather commonly obtained from crude oils that do not contain enough porphyrin to complex even a major part of the vanadium present.... For the

> present, it must be concluded that much of the vanadium of most crude oil is not [emphasis in the original] complexed with substances capable of extraction as porphyrins by current methods. [pp. 395-397]

In every other major review of petroporphyrins or petroleum trace metals, similar arguments are presented based on a wealth of evidence. Sometimes, the arguments are even more damning; thus, Hodgson et al.:[62]

> Porphyrin complexes are subject to attack by other agents.... For example, porphyrin metal complexes may be destroyed to some extent through oxidation if the...oil should come in contact with oxygenated ground waters. It is difficult to assess the magnitude of this possibility since few data are available. Costantinides and Batti (1957) reported that 90% of the porphyrin complexes in an oil were destroyed in a few hours at about 200°C under mild oxidizing conditions.... [p. 250]

We have offered these extracts from authoritative reviews of the literature so that the reader may see for himself the great chasm that separates the claims of those who would use trace metals as passive tags for oil spills from the disinterested appraisals of the scientific evidence. It is perfectly plain (and thoroughly established) that much of the vanadium and nickel in petroleum is water-soluble and volatile. Even the rather stable compounds of vanadium and nickel with petroporphyrins are somewhat subject to oxidation. Moreover:

> Oxidizing conditions usually appear to result in polycarboxylic porphyrin structures rather than the reduced porphyrin side chains characteristic of oil environments.[62]

While the decarboxylated porphyrins are only very slightly soluble in water, the carboxylated porphyrins are known to be rather water-soluble and to have a marked affinity for hydrocarbon-water interfaces.[61, 62] Indeed, Falk[67] has demonstrated an almost linear relationship between the number of carboxyl groups on a porphyrin and the porphyrin's mobility in a solvent system of lutidine and water.

Thus far, we have concentrated our attack on vanadyl and nickel porphyrins because these compounds are known to be rather stable; however, many forms of these compounds are also volatile and water-soluble. It is obvious that volatile, water-soluble compounds are not going to be stable in oil slicks; furthermore, vanadium porphyrins seem to be more stable (to oxidation, replacement, water solution, and evaporation) than nickel porphyrins, so that, as the slick grows older, the vanadium/nickel ratio in the slick will probably get progressively higher.

The notion of using sodium as a trace characteristic in oil slicks is even more poorly advised. Sodium is common in petroleum but it is also the most common cationic metal in sea water; it is therefore readily available to participate in exchange and replacement reactions with the oil slick. The petroporphyrin nucleus is an obvious target for exchange reactions with sodium ions from the sea; unfortunately, these sodium porphyrins are not very stable in the presence of other cations:

> ...Alkali metal ions in porphyrin molecules are readily replaced by small divalent cations, by large divalent cations or by small alkali metal ions.[62] [p. 194]
>
> From studies with lithium, sodium, potassium, divalent lead, mercury, copper, silver, cobalt, magnesium and tin, two rules for the replacement reactions [of petroporphyrins] were formulated: (1) the order of increasing stability is alkali metal, large divalent metal and small divalent metal; (2) the metal porphyrin with the smallest metal is the most stable.[62] [p. 203]
>
> Bonding of protons and metal ions to the [porphyrin] pigment molecule is largely covalent in character..., suggesting that the cation probably does not undergo exchange reactions with cations in solution. Isotope exchange reaction [sic] involving iron, cobalt, copper, zinc, and magnesium complexes verify this with negligible rates.... As would be expected the complexes of porphyrins incorporating monovalent cations show rapid exchange. [Emphasis supplied.] Unfortunately, the exchange reactions with divalent cations were not exhaustively examined; therefore, although negative results were obtained, it is possible that metal complexes of these divalent cations may undergo exchange at low but measurable rates.[62] [p. 203]

Since sodium is a rather small monovalent cation, it will "show rapid exchange" and be "readily replaced" by divalent cations, many of which (e.g., calcium, magnesium, iron, etc.) are easily available in sea water. Other chemical reactions between sea-water sodium and the oil slick may be expected to be more stable; however, one general characteristic of sodium compounds is water solubility, and water-soluble compounds are not likely to remain in an oil slick for very long.

In summary, the trace metals in petroleum make an unreliable "fingerprint," for the fingerprint is very likely to evaporate and be washed away at sea.

3.3 Sulfur-Isotope Ratios

A group at McMaster University in Canada has been studying sulfur-isotope ratios in a variety of geologically important materials (including petroleum)[68] since the late 1940's. Their work has particular value for our purpose because it was not conceived with oil tagging in mind; it was purely a geochemical investigation of isotope fractionation. Thode has summarized[69] the most important arguments and conclusions,[70] which we recapitulate here.

Isotope fractionation is an established and important geochemical process: Ocean carbonate is rich in O-18 with respect to ocean water, plants are enriched in C-12 with respect to atmospheric carbon dioxide, and sea sulfate is rich in S-34 with respect to the sulfur found in meteorites and basic igneous rocks. Although there are nine sulfur isotopes, only four of them occur in natural sulfur (S-32, -33, -34, and -36); all four are stable, but they are not equally distributed: S-32 predominates (95.0%), and S-34 (4.22%) accounts for most of the remainder. The ratio of these two most common isotopes is often standardized with respect to meteorites because this ratio is virtually invariant;[71] in the earth's mantle, however, the content of S-34 varies by approximately 100%. The 34/32 ratio has been studied in many materials, including petroleum and sea water: In sea water the ratio is +20 ±2%, while in petroleum it varies from -8% to +33%—indeed, it varies from -8% to +28% in petroleums from Utah alone, and the apparent significance of this phenomenon has not been lost on proponents of passive tagging.

The fundamental fact in the geochemistry of sulfur isotopes is that S-34 tends to sulfate and S-32 tends to sulfide: S-32 is the more readily reduced and S-34 is the more readily oxidized isotope. The underlying chemical reaction is:

$$H_2(\text{S-34}) + (\text{S-32})O_4^{--} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2(\text{S-32}) + (\text{S-34})O_4^{--}$$

The kinetics of the isotope-exchange reaction are also known: The reaction goes to the right because k_1 is larger than k_2. The equilibrium constant (*K* = 1.071) tells us that at equilibrium, the sulfate will favor S-34 by 71%. Similar calculations show that hydrogen sulfide is 25% richer in S-32 than in S-34. These reactions are not sensitive to either temperature or concentration.

Enzyme-catalyzed reactions, however, are sensitive to both temperature and concentration. For example, when the anaerobic bacterium *Desulfovibrio desulfuricans* reduces sulfate to sulfide, the isotope-fractionation effect is not a constant 25%: It varies from 0 to 25%, depending on conditions.[72] At low sulfate concentrations or at rapid metabolic rates, the diffusion of sulfate is rate-controlling and there is little isotope effect; at slow metabolic rates, however, the kinetic isotope effect approaches

25%. Under the usual conditions of anaerobic reduction in shallow muds, the isotope effects are approximately 15%. The identical argument should also apply when sulfide is oxidized to sulfate by photosynthetic and colorless sulfur bacteria (e.g., the *Thiobacteriaceae*). Although Jones & Starkey[72] could not demonstrate isotope fractionation when *Thiobacillus thiooxidans* aerobically oxidized elemental sulfur to sulfate, they pointed out that:

> This does not eliminate the possibility that there is fractionation during its oxidation of soluble sulfur substrates, but this was not tested.

While all the sulfur compounds in petroleum have not yet been identified, all the identified sulfur compounds are reduced: thiols (mercaptans), disulfides, sulfides, and thiophenes.[73] The ultimate source of this sulfur is not definitely established, but many authorities have argued that it must usually be oceanic sulfate, reduced to sulfide by such bacteria as *Desulfovibrio desulfuricans*; Davis[74] has prepared an excellent summary of the evidence. These bacteria preferentially metabolized the lighter mass isotope, viz, S-32. As we have already seen, this preference is usually around 15%; the 34/32 ratio should therefore be about 15% lower in petroleum than in the sulfates of ancient oceans. The group at McMaster University has shown that this is usually the case; their arguments are compelling:

> Oils from widely distributed pools in the same reservoir rocks, e.g., Devonian, have very nearly the same S^{34} content but differ greatly in total sulphur content.... This constancy of the sulphur isotope ratio for oils formed about the same time, and found in the same formations accompanied by wide variations in the actual sulphur content, is very strong evidence for the suggestion... that as the oils mature and lose sulphur there is little fractionation of the sulphur isotopes. In other words, the sulphur isotope ratio for the oil does not change materially with time but is indicative of the nature of the source sulphur and environment in which petroleum was formed.
>
> ... The fact that oil pools in Devonian rock extending from the 49th Parallel to the Arctic Circle have nearly the same sulphur isotope content indicates that there must have been a large reservoir of sulphur over a large area with a constant isotope ratio in Devonian time and that whatever isotope fractionation occurred in the oil formation process this factor was reasonably constant over the same area. In other words, the conditions of oil formation must have been similar for the whole region. It seems that only a large sea would provide the large reservoir of sulphur uniform in isotopic content and the constant oil-forming conditions. Similar constant conditions and uniform source of sulphur must have prevailed during the formation of the heavy Lower Cretaceous oils and the light Upper Cretaceous oils of Alberta.[68]

There are exceptions and special conditions, and all the evidence is not in, but, stripped of these scientific reservations, the heart of the argument is very small and well worth looking at: Sulfur-isotope ratios are an index of geologic age. Thode et al. as much as say so:

> Six of the crude oils examined from West Texas fields are from Ordovician and Silurian limestone as are four samples from Ontario. . . . It is interesting that with the wide range of sulphur isotope delta-values found for petroleum samples in general that the oils from the Ordovician and Silurian rocks of Texas and Ontario, separated by several thousand miles, should be so similar in their sulphur isotope content. The results suggest a uniform S^{34}/S^{32} ratio in Ordovician and Silurian seas over a wide area.[68]

And Thode himself, after clearing his conscience with a "there-is-some-indication-that," leaves his readers in no doubt

> that the sulphur isotope ratios of the sea have changed with time in a complex, but cyclic, fashion and that the sulphur in petroleum has changed in a similar manner but displaced approximately 15% from the contemporaneous sea level.[69]

S-isotope ratios are just another general index of geological age; geochemists have several such indices (e.g., the ratio of complex cyclic structures to simple chain structures). It is difficult to see, however, how any such index can be of much use in identifying oil spills. For example, our largest foreign source of oil (Venezuela) is a major shipper of Tertiary crude; so is Louisiana, our second most productive oil state. Our second largest foreign source of oil (Canada) sends large quantities of pre-Mississippian crude to our East Coast refineries; so does Texas, our largest oil-producing state. Miocene oil is common in Louisiana; it is also common in Indonesia. Are S-isotope ratios sufficiently precise to distinguish Miocene from Eocene?—if not, oil from Fresno, California, can't be distinguished from the oil of Sanga Sanga, Borneo, or Plaquemines Parish, Louisiana.

There is another objection, however, that may be even more important. The sulfur in oil is reduced, but when oil is spilled at sea, the sulfur is put in an oxidizing environment. Because of kinetic isotope fractionation, the S-34 will be more readily oxidized than the S-32, other things being equal. The logic of this process leads us to conclude that the more the spill is oxidized, the lower its 34/32 ratio will be; a week-old spill should have a lower isotope ratio than a day-old spill from the same source. If the fractionation effect were strong enough, the delta-value might go from highly positive to very negative. It does not seem likely that sulfur-isotope ratios can be depended on to prove a violation of oil-pollution laws.

3.4 Special Cases

While we do not know of any easily identified passive tag that is unaffected by harsh or extended weathering, several kinds of passive tags can be profitably used as presumptive tests on the identity of oil spills under special conditions. These conditions include: infrequent pollution, few possible sources of pollution, no recent pollution, and fresh (single) slicks. In these special cases, chemical analysis does not have to bear the whole burden of proof; the circumstantial evidence (of a non-chemical sort) must be convincing. Ableson[75] is both more and less optimistic than we can be:

> With modern instrumentation, it should be possible to catch the culprits. For instance, a combination of gas-liquid chromatography, controlled pyrolysis, mass spectrometry, and computer calculations probably could provide an identification as valuable as a fingerprint. Patterns obtained from oil slicks could be compared with samples obtained from tankers bound for, and unloading at, United States ports.

If the spill has not been extensively weathered and if there are not many possible sources of pollution, the combination of techniques that Ableson suggests is wasteful: Where the circumstantial evidence is convincing, extensive chemical evidence is not required. However, where there are many possible sources of pollution where pollution is frequent, and where the spill may have been weathered for days or weeks (or mixed with other spills, some of which may have been weathered), it seems highly improbable that any combination of analytical techniques could stand up in court to a carefully reasoned chemical defense. (Some of the chemical objections to metallic and isotopic passive tags were discussed in sections 2 and 3.2-3.3; these are the characteristic objections that might and perhaps should be used by defendants in oil-pollution cases.)

The problem of mixed and continuous pollution is apparently common in Southern California. Ludwig and his associates[76, 77] have reported that:

> Oil and grease from submarine seeps and waste from offshore drilling operations are not of the same worldwide importance but do affect the use of nearshore waters and beaches for bathing and boating in areas located near offshore oil fields. This is especially true along the coast of Southern California where the beaches may be polluted both by natural seepage and by tanker and drilling wastes.

One would expect that similar conditions pertain along much of the Gulf Coast. Moreover, a very recent newspaper account quotes Howard Sanders, a senior Scientist at the Woods Hole Oceanographic Institution, as saying:

> Just in the past few years we're finding we can't sail anywhere in the Atlantic—even a thousand miles from land—without finding oil.[78]

The methods we shall now discuss cannot be recommended for such areas as Southern California, nor for areas that are frequently afflicted by oil pollution; these methods can, however, be recommended for waters that are not near offshore wells, oil refineries, or other possible sources of frequent oil pollution.

In the early 1950's several papers on identification of oil spills were published in the U.S. and England. The first of these (Schuldiner[79]) reported a simple method of paper chromatography that produced evidence for prosecuting and convicting oil pollutors in Baltimore, Maryland:

> A method was found useful in prosecuting harbor pollution violators in Baltimore harbor and in the upper Chesapeake Bay area. It resulted in many convictions and was responsible for periods during which pollutions ceased. This technique was also applied to the identification of the source of petroleum crudes. Various crude, semi-refined, and refined petroleum products give characteristic spot chromatograms by this method.
>
> The simplicity and speed of chromatographic fluorescence analysis, when applied to the field of petroleum products, are easily demonstrated. A spot chromatogram is adequate for identifying the source of crude petroleums and their derivatives. When a crude is fractionated or cracked, a whole series of products is formed, and, as a rule, each derivative will produce a different visual or fluorescence radial pattern. These spot chromatograms identify the complex products formed. Mixtures of petroleum products produce composite chromatograms characteristic of the mixture. [Emphasis supplied.] This fluorescence method and its visual pattern have been applied to the forensic problem of harbor and beach pollution with fuel and lubricating wastes. The source of crude petroleums can be identified similarly.
>
> The government agencies detailed inspectors who obtained samples of oil slick found floating in Baltimore harbor, the upper Chesapeake, and its tributaries. The samples were obtained by tying a string around the neck of a small wide-mouthed bottle, and dragging it across the surface of the oil

> slick. Suspected ships were then boarded. Samples were obtained in 1-ounce wide-mouthed bottles of bunker fuel oils, bilges, a loose oil on the decks or sides of the vessel above the water line, on adjacent docks, fuel intake valves, etc.
>
> Comparison samples should be treated alike. Two or more samples for comparison are placed side by side on the same sheet of blotting paper. It is not necessary to use identical amounts when original materials are compared, but dilutions should be made as accurately as possible. Samples must be protected from evaporation. Changes in viscosity will alter the relative size of the chromatogram structures. [Emphasis supplied.]
>
> A large number of tanker shipments of manifested crudes, imported through the Port of Baltimore over a period of about 3 years, were compared by means of the spot chromatogram method. The chromatograms from known crudes invariably gave identical radial fluorescence patterns. [Emphasis supplied.] These crudes came from many sources, including Saudi Arabia, Kuwait, Iran, Mexico, Venezuela, Romania, Dutch East Indies, and Dutch West Indies.

While Schuldiner's spot chromatograms can be effective, they are not perfect. In the emphasized passages of the preceding quotation, we have underscored three troublesome problems. First, confluent multiple spills will give chromatograms that are characteristic of the mixture, not of the components of the pollution; it is very doubtful that the chemical mixture can be resolved into its legal components, or that a given slick can be proved not to be a mixture unless the circumstantial evidence is overwhelming. Second, any but the freshest slicks may have become quite viscous; they may have experienced considerable evaporation, and their asphaltenes have quite probably agglutinated into a discrete particulate phase; the chromatograms of the slick and the source are likely to differ unless the slick is fresh, and the size of the difference will depend largely on the slick's age. Third, it is not an unmixed blessing that identical chromatograms are invariably produced by known crudes from a given area; if all (or even many) Venezuelan crudes give identical chromatograms, and if two or more tankers carrying Venezuelan crude have recently been in the area of a spill, it is not clear how one ship rather than the other could be blamed.

In 1953, two years after Schuldiner's work appeared, Herd[80] reported that he had used paper-strip chromatography to identify fuel oil that had been spilled in the harbor of Wellington, New Zealand. Herd neither cited nor showed any familiarity with Schuldiner's paper. Nevertheless, Herd's claims are quite similar to Schuldiner's:

> **On numerous occasions samples of fuel oil collected from the surface of navigable waters have been submitted to us for comparison with samples of fuel oil collected from the tanks of ships suspected of having made the discharge in contravention of the Oil in Navigable Waters Act. To obtain incontrovertible evidence by the conventional methods of oil analysis that such samples are identical is almost impossible. The sample from a river has usually lost some of its more volatile constituents and, in addition, it will often be emulsified to a certain extent with water. The removal of this water by drying, filtration or solvent extraction results in a product whose analytical characteristics are significantly different from those of the original oil.**
>
> Attempts to prepare evidence of identity that could be demonstrated visually by the use of adsorbent columns and by the normal technique of paper chromatography did not produce results of the required degree of precision. The paper-strip method here described, however, gives visual evidence of complete identity or of non-identity and, if necessary, the strips can be used as evidence in a court of law.

All the reservations that apply to Schuldiner's methods apply just as strongly to Herd's. One further reservation merits special attention. Herd's methods "identify" only the ether-soluble portion of the slick. Although the ether-insoluble fraction of a slick is admittedly difficult to work with in the analytical laboratory, it can provide valuable information (see, for example, section 4. 3. 2); in any event, it does not seem prudent to ignore it altogether because it can be a sizable fraction of the slick. Ludwig & Carter[76] have reported that 12 crude oils contained (on the average) 7. 9% ether-insoluble material, that some crude oils contained as much as 15. 5% of ether-insolubles, and that one oil film collected at a beach near Santa Barbara contained 6. 5% ether-insolubles.

Chromatographic methods are relatively simple and cheap. Other methods, however, may also be used if there is sufficient equipment at hand and if the circumstantial evidence is already convincing. In section 3. 2, for example, we discussed Johannesson's method[81] of identification, which was based on analysis of vanadium and nickel. Obviously, Johannesson's methods could be very much improved. Canevari,[82] for example, has suggested emission spectroscopy, and Guinn & Bellanca[83] have suggested neutron-activation analysis for determining trace metals in oil spills. While we think that none of these methods can conclusively and reliably identify oil spills by analyzing only the oil slick, Ciuffolotti et al.[84] have demonstrated that neutron activation is more accurate than either spectrography or spectrophotometry:

> A comparison between neutron activation data and those from spectrographic and spectrophotometric analysis, limited to vanadium and nickel, was made. The results ... indicate, in general, that higher concentrations of vanadium and nickel were found by the neutron activation method. These higher values are believed to be closer to the real contents of these trace metals, since the neutron activation procedure described does not require drastic thermal treatment which may lead to partial loss of the elements.

McCoy[85] had argued against spectrographic methods as early as 1962, particularly for nickel analysis:

> It will be noted that there is evidence of volatility of nickel even in these heavy residual materials. The lowest results were obtained by the spectrographic method which involves direct ashing...

McCoy's data show that spectrographic determinations of nickel in residual fuel oils are about 30% lower than colorimetric determinations, and about 20% lower than gravimetric determinations.

Other methods of passive tagging (such as isotope ratios) might also prove suitable, but —again— there is every reason to believe that the chemical evidence alone would not be conclusive. All methods of passive tagging entail this risk, but the risk seems well worth taking in those special cases where the circumstantial evidence is powerful.

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SECTION IV

ACTIVE TAGGING

4.1 General

Literature studies have revealed that it is extremely difficult, if not impossible, to assign, unequivocally, liability for an oil spill solely on the basis of identification of the intrinsic constituents (organic or inorganic) of the spilled oil. The preceding presentation has emphasized these difficulties. How then can the violator be identified from evidence provided by the oil slick? For if the intrinsic components of the oil slick do not lend themselves to reliable identification, possibility of introducing suitable additives (active tags) must be considered. What does one require of an active tag? Ideally, it should satisfy ten criteria.

1. It must be an unusual material that is never found in the environment and is found only in the petroleum to which it has been added.

2. It must be compatible with (i.e., chemically unreactive and physically stable) and soluble or dispersible in the oil.

3. It must be both insoluble and nondispersible in water.

4. It must be relatively involatile.

5. It must be stable to chemical, photochemical, and microbial degradation in the oil-slick environment.

6. It must be easily detectable in extremely small quantities by readily available analytical techniques.

7. It must allow for modifications so that, when it is added to a particular oil shipment, it provides a unique code or "license plate" for that carrier or transporter.

8. It must remain with the oil during the course of its history following a spill.

9. It must in no way interfere with the end-use applications for that oil, nor complicate further processing and refining.

10. It must be available in quantity at economical prices.

While few tags will be ideal, all candidate tags must satisfy all criteria to some degree.

4.2 Soluble Tags

4.2.1 Halogenated Aromatics

One particular class of compounds that satisfies most of these parameters, from a theoretical standpoint, are the polynuclear, aromatic hydrocarbons; specifically, the halogenated aromatics.

Over the past several decades, many studies have been performed which were aimed at identifying and characterizing the major constituents of petroleum.[86] Although many types of aliphatic, aromatic, and heterocyclic compounds have been identified, there is no evidence of the presence of halogenated, polynuclear aromatic compounds in crude oils. Because of this uniqueness these substances appear extremely attractive for use as a label or tag for crude oils. Let us now examine the properties of these aromatics to see if they could potentially satisfy the remaining criteria listed above.

Stability

It is well known that the aromatic series of hydrocarbons is significantly more stable to oxidation, compared to the aliphatics, because of the conjugated structure of the aromatic ring.[87] A conjugated compound, a compound which resonates between two or more structures, is actually more stable than any one of the possible valence-bond structures. This stability is due, in part, to the resonance and bond-dissociation energies of the aromatic system. Table 2 compares the resonance energies of some aromatic compounds.

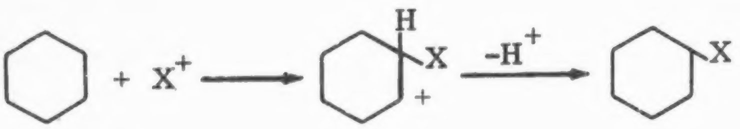
TABLE 2

RESONANCE ENERGIES OF SELECTED AROMATIC COMPOUNDS[88]

Compound	Kcal/mole
Benzene	37
Naphthalene	75
Anthracene	105
Phenanthrene	110

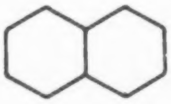
The series is characterized by a marked increase in the resonance energy as the number of rings increases, and this increase is paralleled by a marked and progressive increase in the stability of the derivative. In addition, the resonance energy is somewhat greater for the nonlinear ring systems than for the linear ones; the former resonating among more stable valence-bond structures than the latter. The heterocyclic compounds on the other hand have substantially lower resonance energies and correspondingly lower stabilities.

Halogenation of the aromatic compounds has in common with nitration, sulfonation, and acylation the great advantage of stabilizing the ring against further attack.[89] The mechanism of the reaction, involving electrophilic substitution, involves attack of the ring by a positive halogen atom followed by a loss of a proton, as shown below.

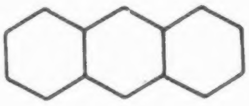


An important feature of the use of halogenated polynuclear aromatic hydrocarbons is that there are many different ways to substitute F, Cl, Br, or I and their combinations, on the aromatic nuclei, thus providing a large number of specific tagging compounds.

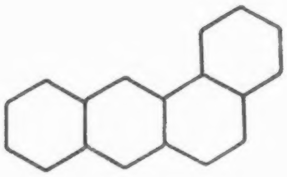
The structures below depict only some of the vast number of stable polynuclear ring systems that can be considered for halogenation:



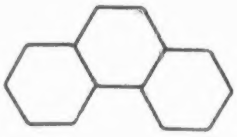
Naphthalene



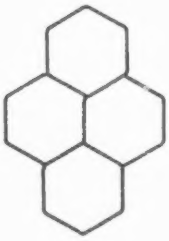
Anthracene



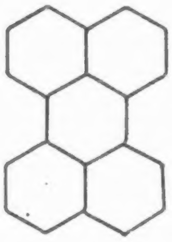
1, 2-benzanthracene



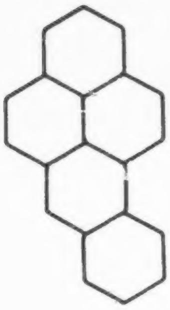
Phenanthrene



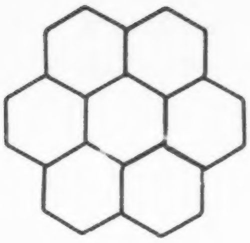
Pyrene



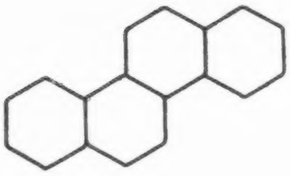
Perylene



3,4-benzopyrene



Coronene



Chrysene

Depending on the particular polynuclear hydrocarbon, a large number of mono-, and polysubstitution isomers can be produced with F, Cl, I, and Br. For example, naphthalene alone has two isomeric monosubstitution products ($C_{10}H_7X$), ten isomeric disubstitution products of the type $C_{10}H_6X_2$, and fourteen of the mixed type (with any two halogens) $C_{10}H_6XY$. And a greater number of combinations are obtained with the tri- and octa- substitution isomers.

The table below lists the 40 fully identified, but not all the theoretically possible, di- and polychloronaphthalenes, for example.

TABLE 3

CHLORINE ISOMERS OF NAPHTHALENE[90]

1:2
1:3
1:4
1:5
1:6
1:7
1:8
2:3
2:6
2:7
1:2:3
1:2:4
1:2:5
1:2:6
1:2:7
1:2:8
1:3:5
1:3:6
1:3:7
1:3:8
1:4:5
1:4:6
1:6:7
2:3:6
1:2:3:4
1:2:3:5
1:2:3:7
1:2:4:6
1:2:4:7
1:2:6:8
1:3:5:7
1:3:5:8
1:3:6:7
1:4:5:8
1:4:6:7
1:2:3:4:5
1:2:3:4:6
1:2:3:5:7
1:2:3:4:6:8
1:2:3:4:5:6:7:8

All of the above compounds have boiling points in excess of 250° C. The stability of overcrowded halogen compounds (e.g., octachloronaphthalene) has also been demonstrated.[91] The total number of combinations obtainable when considering the fluorine and bromine or iodine substituent on the same molecule as the chlorine, provides (in the thousands) individual compounds which are easily distinguished from "background" polynuclear hydrocarbons naturally present in the petroleum. In addition, because of the halogen substituent, each isomer can be readily identified in parts per billion within a mixture by electron-capture gas chromatography.

This provides, then, a large series of compounds which can be used in tagging a large number of separate petroleum samples, each tag being unique to that particular sample. Since the aromatics are soluble only in the petroleum hydrocarbons, they would remain with the oil slick and would be recovered with a water grab sample. In addition, halogenation of heavy condensed, aromatic compounds of the naphthalene type (and higher: anthracene, phenanthrene, perylene, pyrene, coronene, etc.)92 would ensure their involatility since the tag must remain with the heavy petroleum fraction (Table 4). In addition, halogenation lowers the vapor pressure significantly.

TABLE 4

VAPOR PRESSURES OF SOME SELECTED AROMATIC POLYNUCLEAR HYDROCARBONS FOR USE AS TAGS (25 to 50° C)[93]

Compound	Vapor Pressure (mm/Hg)
Benzene	26
Hexachlorobenzene	$\ll 1$
Iodobenzene	~ 1
Fluorobenzene	100
Anthracene	$\ll 1$
Naphthalene	$\ll 1$
Phenanthrene	$\ll 1$

Active tags must be identifiable within the residuum or asphaltenic fraction of the spilled oil even after several weeks of exposure and weathering. Petroleum alphaltenes have a polycyclic structure, comprising mostly aromatic rings[94] in a pericondensed sheet configuration.[95] In general, this material would present a considerable background problem. However, the analytical technique suggested for the detection of the halogenated, polynuclear aromatics (discussed in the following section) should minimize this problem.

Electron-Capture Gas Chromatography for Halogen Compounds

An attractive feature for using the halogenated, polynuclear hydrocarbons as tagging compounds is that the halogen substituent can be readily detected and identified both qualitatively and quantitatively by gas chromatography using the electron-capture detector.[96] The electron-capture detector is a substance-specific device that is sensitive to certain types of molecules containing electrophilic atoms or groups such as halogens, carbonyls, nitro-groups and certain condensed-ring aromatics, metals, etc.[97] It has a very low sensitivity for hydrocarbons other than the aromatics.[98] Furthermore, and very important, the electron-capture detector is extremely sensitive to the halogen substituent. It can reliably detect halogenated hydrocarbons present in a sample in quantities as low as 10^{-4} to 10^{-6} mg/l[99] and, under optimized operating conditions, a projected sensitivity to 10^{-10} mg/l has been reported.[100] Electron-capture gas chromatography has been used successfully to determine ppb concentrations of chlorinated insecticides in waste water samples,[101] and chlorinated hydrocarbons in air samples.[102] Since gas chromatography has been used extensively to separate and characterize the components of petroleum and oil products,[103] it can be utilized with great reliability and precision to separate the components of a spilled oil sample; coupled with the extreme sensitivity offered by the electron-capture detector, gas chromatography can ascertain the presence of an added tag by virtue of its chemical structure and substituents. This latter aspect can most readily be performed by prior compilation of a catalog of standardized chromatographic column retention times of the various tagging compounds. When an oil spill sample is brought in for analysis, the retention times of the various chromatographic peaks of the sample are compared with the catalog and the proper component peaks identified. The correlation between chemical structure and column retention times (or elution values) is well documented.[104] Halogenated aliphatics,[105] heterocyclic compounds, and nonhalogenated, polynuclear aromatics as well as inorganic halogens should not interfere, since these compounds either will not have the same retention times on the gas chromatographic column as the tagging compound or will not be detected because of the selectivity of the electron-capture detector. If several peaks should occur near or overlap the one of interest, these particular fractions can be collected and re-chromatographed under operating conditions that will give better separation.

Because of the great sensitivity of the electron-capture detector to halogenated compounds, it should be evident that very little of the tagging material is necessary to tag a large volume of oil. For example, the largest tankers now on the drawing board will hold 500,000 tons of oil. How much tag must be added to identify such immense cargoes? The practical limit of detection by electron-capture gas chromatography is now 10^{-12} gm/gm. Therefore, 0.016 ounce of halogenated tag is (theoretically) sufficient to tag a half million tons of oil. But why push the limit of detectability? Why not allow a safety factor of three orders of magnitude? Why not, indeed, because then only 1 pound of tag (about 1 pint) will safely do the job. And just how safe is "safely"? One gram of oil slick (about 0.25 ounce) will contain one nanogram of tag, and one whole nanogram of tag is extremely easy to detect by electron-capture gas chromatography.

It is not without interest that electron-capture gas chromatography is several orders of magnitude more sensitive than emission spectroscopy[106] and approximately two to three orders of magnitude more sensitive than neutron activation techniques.[107] By combining gas chromatography and mass spectroscopy[108] the halogenated, polynuclear, aromatic tags can be absolutely identified. Just as important, because of the sensitivity of the electron-capture detector, the tag can be used in extreme dilution; the tag can therefore be added to the oil in amounts of orders of magnitude below the level which will not interfere with the end-use applications of oil or oil products.

In the preceding discussion we have pointed out the potential applicability of utilizing halogenated, polynuclear aromatic hydrocarbons as tracers for identifying the perpetrator of an oil spill. We have considered their usefulness in terms of the criteria that an ideal tag must possess to be practicable, and the suggested soluble tags appear to meet these criteria. As was mentioned earlier, it would be extremely difficult to identify a particular petroleum solely by virtue of its intrinsic constituents because of the differences in the stability of these various components to weathering. This consideration arises when any chemical compound is to be exposed to weathering and especially applies to the halogenated aromatics considered here as potential tagging compounds.

Stability of the Tag to Oxidation

It is generally acknowledged that the fate of many of the classes of aromatic compounds, naturally present in petroleum exposed to aging, is condensation or polymerization of the aromatic rings together with naphthenic compounds into high molecular weight compounds. This hybrid material is commonly referred to as the asphaltenic fraction of the petroleum. Although there are other fractions of high molecular weight in petroleum (such as the resins and the maltenic fraction), the asphaltenes appear to have the highest aromatic carbon content.[109] The mechanisms responsible for this condensation may be analogous to those in which it was found that heating for 30-40 hours at 300-350° C resulted in fairly rapid formation of condensed aromatic systems from the homologues of benzene, methylnaphthalenes, and from bicyclic aromatic hydrocarbon fractions isolated from various crudes (Romashkino, Radchenkovo, Khaudag).[110] During this thermal processing of the petroleum, the peripheral parts of the molecules are destroyed, and the alkyl substituents are split off the aromatic nucleus; this is accompanied by condensation reactions of the cyclic parts of the molecule with the formation of progressively condensing polycyclic compounds.[111] The idea that oxidation such as the above may have been responsible for the conversion of petroleum to asphalts rests on the observation that, in certain oils, the presence of an asphalt deposit seems to be related to the migration of an asphaltic petroleum from depth to the earth's surface where it becomes exposed to evaporation and atmospheric oxidation.[112] Since it is known that aromatic hydrocarbons are extremely difficult to oxidize at low temperatures and pressures,[113] atmospheric oxidation is most probably a result of photochemical action. That this atmospheric oxidation and polycondensation does occur is evidenced by the fact that the weathering of petroleum results in the accumulation of a tarry residue rich in condensed aromatic nuclei.[114]

What then could be expected to happen to a halogenated, polynuclear aromatic tagging compound which has been incorporated into a petroleum sample and exposed to air, water, and light for extended periods of time? It was discussed previously that, as a class of compounds, the aromatic structures are extremely stable to oxidation at ambient temperatures and pressures.[115] That is, a significant degree of oxidation can take place only at temperatures considerably higher than ambient and preferably in the presence of specific catalysts. Furthermore, halogenation has the added effect of stabilizing the aromatic nucleus to attack. We saw earlier that unsubstituted polynuclear aromatic hydrocarbons can add oxygen, initiated by photochemically generated radicals, across the central ring to give the transannular peroxide,[116] and that the presence of electron-donating groups (such as methyl or phenyl) at the reactive centers facilitates this reaction with oxygen. However, because of the presence of halogen substituents, the very opposite of electron donors, the general reactivity (oxidation and condensation) of the polynuclear aromatic tag will be substantially less than that of the condensed aromatic compounds naturally present in the oil, often in large quantities.

Stability of the Tag to Microbial Oxidation

In an earlier section of this report, the microbial utilization of various types of petroleum hydrocarbons was discussed. These hydrocarbon types encompassed aliphatic (straight and branched) and aromatic (with straight and branched side-chains) compounds. Whenever the microorganism demonstrated ability to oxidize the particular hydrocarbon substrate, that compound was not of the halogen-substituted type. In fact, the presence of an electron-donating group such as a methyl group sometimes facilitated microbial oxidation of either the alkyl side-chain or the ring itself. Therefore, for the same reasons that were invoked for the nonreactivity of the halogenated, polynuclear aromatics to photochemical oxidation, viz, the presence of highly electrophilic halogen substituents, it is believed that the microorganisms indigenous to petroleum and sea water will not attack and oxidize the tagging compound. In general, the aromatic hydrocarbons are more inhibitory to cell growth than are the paraffinic or cycloparaffinic hydrocarbons.[117]

The intermediates detected in aromatic hydrocarbon oxidation have been studied in investigations on the degradation of aromatic compounds by microorganisms that are not hydrocarbon oxidizers per se.[118] It is therefore assumed that no significant degree of microbial oxidation of the halogenated, polynuclear aromatic tagging compounds will occur.

Advantage of the Soluble Chemical Tag

The foregoing discussion has attempted to formulate a working hypothesis for the identification of the perpetrator of an oil spill. This hypothesis requires that a tagging chemical which most ideally meets the criteria set forth previously be added to the oil cargo. These tagging chemicals are the halogenated, polynuclear, aromatic hydrocarbons. The single most advantageous feature of these compounds (indeed, of all active tags) is that they potentially enable identification of the pollutors in a situation where multiple spills of oil occur at the same location. Under these circumstances considerable mixing of the various oils will occur. Since a large number of halogenated compounds are available or can be synthesized, each oil to be transported can be labeled with its own unique, single compound. In the event of multiple spills, a water grab sample will contain the tags of all the labeled oils. Since gas chromatography can resolve the individual tags according to molecular structure,[119] identification of the violator, even under these conditions, is quite possible.

A combination of materials (soluble or nonsoluble) to label a single oil, although unique for that particular oil sample, creates complications in multiple spills, where the various fractions and constituents of the oil including the tags will be well mixed.

In actual practice, it may be necessary to perform a preliminary concentration and fractionation of the recovered petroleum sample to optimize tag analysis and to separate the aliphatic fractions from the aromatic fractions (also, to remove water). These preliminary steps would facilitate chromatographic processing for detection and identification of the tagging compound by considerably reducing the background peaks which would appear on the chromatographic profile. Since interest lies only in the aromatic fraction, this preprocessing might, in actuality, be highly desirable (although not essential, because electron-capture detector is not sensitive to unsubstituted aliphatic hydrocarbons). In addition, the column parameters and chromatographic processing would be made simpler, since a narrower range of compounds would have to be separated. In some cases, where a large amount of the recovered petroleum sample is in the form of a water-in-oil emulsion, the emulsion would have to be broken and the oil separated from the water prior to chromatographic analysis; of the several techniques for resolving oil-water emulsions, addition of an appropriate surfactant in combination with froth flotation is the least expensive and simplest method for processing large quantities.

Cost Considerations

It is desirable to devise oil tagging systems that are relatively economical to prepare and use; however, low cost is not always essential to the system's implementation and effectiveness, and we believe that, in this case, the resultant benefits far outweigh and justify the initial costs.

In evaluating the cost of commercially prepared halogenated, polynuclear hydrocarbons, we found that many derivatives are inexpensive while others are relatively expensive. The table below illustrates the wide price range of some selected halogenated derivatives.

TABLE 5

UNIT PRICE OF SEVERAL SELECTED HALOGENATED AROMATIC HYDROCARBONS

Compound	Price/Lb
Monochlorobenzene	$ 1.10
Bromobenzene	2.60
Hexachlorobenzene	2.50
1,2,4-Trichlorobenzene	1.30
1,4-Dichlorobenzene	1.10
1,4-Dibromobenzene	3.50
Monofluorobenzene	18.00
1,3,6,8-Tetrachloropyrene	30.00
Iodobenzene	24.00
Bromofluorobenzene	116.00
2-Fluoronaphthalene	360.00
1-Bromo-2,3,5,6-Tetrafluorobenzene	700.00
9-Bromoanthracene	1000.00

The prices of several of these derivatives, though high, are not disturbing if it is recalled that extremely small amounts are needed to tag a particular oil cargo. Approximately 0.001 lb of the chemical can be detected by electron-capture gas chromatography in 100 million lb of oil (100 million lb = 50,000 tons). Using 9-bromoanthracene, for example, the material cost of tagging 50,000 tons of oil would be $1.00. If other halogen derivatives of anthracene are comparable in price, then 1000 tankers carrying 50,000 tons each can be labelled for a material cost of $1000. If one then considers that a single major spill can cause damages amounting to many millions of dollars, a cost of $1000 to tag a thousand potential pollution sources becomes insignificant by comparison. If we consider this in terms of the number of transporters to be tagged, we find that, in 1966, there were approximately 3000-4000 tankers (2000 gross tons and greater) and approximately 2000-3000 miscellaneous types of petroleum-carrying vessels (less than 2000 gross tons) traveling the waterways of the continental United States. Let us assume, for ease of calculation, that at present there are 10,000 vessels, having an average capacity of 1,000,000 lb of crude and semi-processed petroleum. Since we know that the halogenated polynuclear aromatics can undergo a dilution of 10^{12} and still be detectable, then, 1 x 10^{-6} lb of tag can be added to 1,000,000 lb of oil. However, if a dilution factor of 1000 is introduced because of potential spillage and losses during sample recovery, then 0.001 lb of material can be used to tag the average vessel. This means that even if the cost of every tagging compound is $1000/lb (which is extremely unlikely), an average materials cost of only $1.00 per vessel would be incurred. Conversely, if the cost of every tagging compound is initially $1.00/lb (equally unlikely), then it would cost only 0.1¢ per vessel. We believe that, in practice, the materials cost per vessel would be somewhere between these two estimates.

4.2.2 Organometallics

Halogenated aromatic molecules are not the only attractive class of oil-soluble tags. In 1962, a group at the National Bureau of Standards, in collaboration with the American Petroleum Institute, developed a number of stable, oil-soluble organic compounds (mostly organometallics) for use as analytical standards in the spectrographic analysis of petroleum products.[120] The trace elements include Al, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, P, K, Si, Ag, Na, Sr, Sn, V, and Zn; as cyclohexanebutyrates and/or ethylhexanoates, these metals make spectrographic standards that have the following properties: Each is reproducible, stable, nonvolatile, oil-soluble, and compatible with all the other spectrographic standards in this series. Many of these metals can be detected spectrographically in extreme dilution (parts per million or less), so that one gram could be used to tag a ton or more of petroleum. The 28 compounds that were selected as standards were chosen from an initial list of over 150 candidates; many of the candidates that were rejected as spectrographic standards may still be useful as active tags for oil spills: One of the principal reasons for rejection was extreme chemical purity (e.g., the metal naphthenates), and this requirement might be somewhat relaxed for oil-spill tags. These 28 standard samples, prepared in solid form for easy weighing and handling, may be purchased for $2.00 a gram from the National Bureau of Standards. Obviously, in mass production (with some relaxation of the requirements for extreme chemical purity), the price might be significantly reduced.

Even though all this work on spectrographic standards has made the use of certain organometallics an attractive possibility, there are still several problems and doubts that must be resolved. First among these is the problem of solubility. Only a few of the Bureau of Standard's organometallic standards could be dissolved in oil, without heat or other solvents. If the standard were dissolved in a solubilizing agent (such as a free carboxylic acid, a diketone, or an ester) and then diluted with the base oil, however, the resultant solutions had optimum stability and highest concentrations of trace metal. The solutions were judged satisfactorily stable if a solution of at least 500 ppm of the trace metal of interest remained "clear and devoid of visible change during several weeks at room temperature."[120] An excellent solubilizer and stabilizer was found to be an equimolar mixture of bis(2-ethylhexyl)-amine and bis(2-ethylhexyl)dithiocarbamic acid in an equal volume of xylene. It is not clear, however, what the highest stable concentration of metals might be:

> A precise determination of the maximum concentration attainable for each element of interest, either individually in oil plus solubilizers, or as a mixture of the standard compounds in oil plus solubilizers, has not been made. However, solutions having concentrations much higher than those given have been prepared and found to be stable. [Emphasis in the original.] All solutions prepared from the standard compounds (according to the directions given) have, up to this time, shown no signs of deterioration on keeping.[120]

A related question is more important still: What happens to the analytical standard once the solubilizers and stabilizers have evaporated, as is likely after a slick has aged on the sea for several days? Will the standards gel or precipitate? It is known, for example, that several organometallic salts are used in the pigments of paints for ships.

A second major problem is background: Most crude oils contain traces of inorganics (especially metals), and some crudes have more than 0.5% ash; there are several excellent reviews of the literature on this topic.[121] Many refined petroleum products also contain metals, either deliberately added (e.g., components of additives to impede corrosion and oxidation or to improve lubricating properties), or adventitiously present (e.g., volatile organometallics in the crude that were not removed during refining). How can this background be distinguished from the active tag? Analysis of petroleum shipments for the presence of background interferents is obviously not the answer: — It is much too costly, for one thing, and for another there is no guarantee that the metallic suites in the oil slicks will be identical to those in the unspilled oil. Indeed, there is every reason to believe that the suites will be drastically different (see section 3.2 of this report for a discussion of this matter). A better solution is to separate the tag from the slick (by chromatography, for example) before attempting further identification. Since the tag is a chemically stable "known," and since the organic moiety of the tag (e.g., nothing like a cyclohexanebutyrate is mentioned in any recent comprehensive review)[122] should be rare in petroleum, there is no reason to believe that background suites will invalidate this method of tagging. However, separating and concentrating the tag from each slick sample adds to the time and cost of identification; since there are several thousand oil spills in U.S. waters each year (see section 1 for a discussion of the evidence), the problem of time and cost is not inconsiderable.

4.2.3 Summary and Conclusions for Soluble Tagging

The preceding sections have, in some detail, considered the use of soluble chemicals as tags for oils. A large number of chemical species may be detected in oils, and a large number of stable chemicals are available which are not naturally present in petroleum in parts per billion or more; such materials represent the two basic possibilities for oil tagging: passive and active, respectively. Chemical tags are, of course, already used in many ways: for tracing the flow of fluids through the body in medicine, in tagging materials for the study of transport phenomena in engineering, and in radiochemically analyzing reaction kinetics in chemistry. The following paragraphs present the general conclusions which have been reached regarding chemical or soluble tagging of petroleum.

- Passive tagging ("fingerprinting") is not practicable in the cases where it is most critically necessary.

- Active tagging is, in principle, quite generally applicable.

Passive chemical tagging should be rejected because of the following:

a. Oils, as the term is usually meant, contain a large number of chemical species. To characterize an oil completely would require that all species be quantified down to the limits of detection (say parts per billion or less); as general analytical and control procedures such quantifications are totally unreasonable.

b. Certain individual constituents of oil have been suggested as possible tags in their own right; without exception, it has been found that the attempted use of such tags would be fraught with difficulties which at this time appear insurmountable. Detection of specific trace materials (e.g., sulfur isotopes or metal porphyrins) to aid in the apprehension of small carriers which have made small spills is not possible since detection sensitivity is much too low.

c. The effect of weathering on spilled oil is known to be severe; on the other hand, there is presently no way in which this effect can be accounted for. Since an identification technique is sought which can be applied to smaller carriers and small slicks of unknown age, weathering in and of itself tends to rule out the passive tagging ("fingerprinting").

d. Perhaps the biggest problem with the passive tagging techniques is that oils from the same geological area and era tend to be very similar in chemical composition; the errors inherent in chemical analyses generally make any marginal differences in such oils impossible to detect. Anyway, an additional labeling method would still be necessary if similar oils were the responsibility of different carriers.

e. In the case of passive tagging, identification of a particular oil would necessarily involve errors which would be compounded for multiple spills; obviously, mixing of similar oils would result in an insoluble dilemma. This inherent difficulty would, in turn, be compounded by the effects of weathering, cargoes of mixed oils, and the complexity of the oil transport system.

Active chemical tagging, however, should for certain cases be considered carefully. The following reasons pertain:

a. Certain stable chemicals are available which are not known to exist naturally in petroleum (e.g., organometallics and halogenated polynuclear hydrocarbons); these chemicals can be obtained in very well-characterized forms for from cents to thousands of dollars per pound. Detection sensitivity sets the amount necessary in any particular application.

b. Since the chemicals to be used as active tags are readily soluble in oils, there is little chance for problems in mixing or adding trace materials to oil cargoes; trace amounts of such chemicals added to fuel or crude oils would not have deleterious effect(s) as far as either producers or consumers are concerned.

c. Characterization may be as specific as necessary provided that provisions are made for tagging the cargo of each potential (and relevant) polluter; this necessitates that a large number or family of detectable compounds be available (this is certainly the case for the halogenated polynuclear hydrocarbons, for instance).

d. Given that point c. is fully complied with, the problem of multiple oil spills could be resolved.

e. Production of organometallics and halogenated polynuclear hydrocarbons is well known; in fact, many of these compounds are available as standard reagents or can be readily synthesized on order.

f. The necessary analytic techniques are available; among these are spectrophotometry, gas and paper chromatography, and neutron activation; the sensitivity of these various methods must be kept carefully in mind (little problem is expected with the halogenated polynuclear hydrocarbons (detectable in the parts per trillion range) while existing techniques for the organometallics appear to be an order of magnitude or more from what they should be).

Certain problems can arise with respect to these techniques, however; among these are:

a. Little is known of the effect of weathering on these materials while they are contained in an oil slick; it is not unreasonable to postulate that halogenated hydrocarbons might show a preference for sea water over a relatively nonpolar oil media.

b. Smaller concentrations of trace materials might necessitate samples of spilled oil which are too large to be obtained practically, while in the laboratory they might require complex preconcentration procedures.

c. In the absence of preconcentration, detection (especially for the organometallics) could be extremely difficult for reasonable bulk quantities of trace materials. For instance, a detection sensitivity of one part per million would require that 200 pounds of tagging material be added to a 100,000-ton tanker; this could be quite a costly amount of material as compared to grams per tanker for halogenated hydrocarbon and particulate tags.

d. There is considerable public opposition to the use of halogenated hydrocarbons in situations where they may be transferred to the environment. However, the toxicity to marine life of halogenated polycyclic hydrocarbons has not been established. This contrasts sharply with the halogenated aliphatic hydrocarbons (pesticides).

Point a. could be resolved by appropriate feasibility studies while b. and c. obviously depend upon the selection of the right tagging material(s). Point d. can be resolved only through education of the public as to the harmless nature of trace quantities of halogenated polynuclear hydrocarbons (less than one part per billion).

4.3 Particulate Tags

4.3.1 Introduction

As with soluble chemical tagging of petroleum, insoluble particles may be used for both active and passive techniques. Passive particulate tagging, however, is much less attractive (upon cursory examination) than passive chemical tagging. Although the particles naturally present in crude petroleum can convey a wealth of information to a careful investigator, their relatively small number and wide variety preclude a statistically reliable identification of a given crude. Other factors also invalidate identification: The entrainment of new particles during transport of the oil, the addition of particulate matter (especially pollen and spores) during exposure to the atmosphere; the sometimes fragile and ambivalent nature of the solids contained in crudes; and the fact that much of the particulate material in crude oils is in the form of asphaltenes, which are identified as suspended solids, colloidal particles, and/or solute molecules, depending upon the investigator and his techniques. Petroleum geologists, palynologists, and engineers have shown some interest in the particles that naturally occur in crude oils; they will probably continue to do so in the future. However, their interest does not appear promising of a technology for oil tagging.

Adding well-characterized particles to crude oils (active tagging) is, on the other hand, a promising technique. In the first place, present technology can easily manufacture such particles; in the second, they can be added to oils in small quantities; and, in the third, there is good evidence that, if the need arises, they can be isolated from the oil matrix in quantities sufficient to allow a very specific identification. It is important to note at this point that active particulate tagging has all the advantages of oil-soluble active tags (e.g., specificity and small amounts of tagging material) as well as several that make it more suitable. Foremost among these latter is the ease with which such particles may be produced using the same basic technique (e.g., grinding and spheroidizing of solids produced from an appropriate liquid melt).

4.3.2 Palynological Studies

Although palynological techniques have been used in the oil industry for about 20 years,[123] there is still only a small amount of information on the particles in crude petroleum. The references accompanying this report contain, we believe, all the pertinent studies which relate to this subject and which are generally available; this was borne out by people in the oil industry. Unfortunately the oil industry has less interest in the nature of the solids found in crudes than in the various organisms and fossils in a given stratum or zone, that might lead prospectors to oil. In fact, most of "palynology's first 20 years" in the industry has been to aid prospecting. The rare exceptions have been those few petroleum geologists who have studied the particles in crude oil in an effort to explain its genesis. For obvious reasons there is little impetus for financing such studies.

4.3.2.1 Petroleum Geology: It is interesting to note that what appears to be the most definitive study on the nature of the particles in crude oils is also the first. J.M. Sanders[124] in his 1937 paper presented a detailed analysis of his methods and results for a large number of Mexican and Rumanian crudes. This paper stands as *the* basic reference to this day. Although it is popular to refer to such studies as palynological, Sanders and others have also found fragments of tissue, hairs, microalgae, bits of feathers, microfossils, etc. Other than for slightly more specific data, recent studies have added little to his general conclusions. Sanders was interested in the crude-oil microfossils in their own right; he attempted to explain petroleum genesis by considering the fossil evidence. Most studies, however, have been aimed at petroleum exploration.

In 1941 Waldschmidt[125] reported on examinations of the organic residues from Permian crude oils. His techniques were apparently very similar to those of Sanders, but already the motivation for such studies was moving toward correlation with particles outside of oil deposits rather than of the nature of those occurring naturally in them. Within the oil industry such a movement continued. By the 1960's studies[126, 127, 128] of the organic microparticles in crude oils had evolved into studies of asphaltenes (asphaltic particles). These materials are of considerable interest in the oil industry but of little value as well-characterized microsolids; they, in fact, are highly ambiguous in their properties. For instance, the residue from petroleum distillation at 350°C (1 to 40 wt %) is the asphaltic fraction; the part of this residue which is insoluble in normal-pentane is by definition the asphaltenes (1 to 15 wt %). Further, the portion of the latter which is insoluble in carbon tetrachloride is called the carbenes (0.3 to 1.0 wt %); this will be of more interest later. Materials isolated in this manner from a substance as complex as crude petroleum can be expected to be complex also. In fact, the "particles" so refined are small (about 50 Å diameter and 1000 to 10,000 molecular weight), spherical, hard to centrifuge, hard to oxidize, and almost impossible to identify in any exact sense of that word. These facts defeat any reasonable use of asphaltic particles as oil tagging materials and, in fact, indicate that they are really macromolecules which behave as solutes, colloids, or suspensoids, depending on how and for what they are being studied. Sergienko dismisses the portions of the asphaltic fraction which are insoluble in carbon tetrachloride (the carbenes) and in carbon disulfide (the carboids) as unimportant. This is not surprising. The asphalt industry would benefit little from a more exact delineation of the molecular nature of asphalt. Sergienko's lack of interest is manifest in his claim that there are no particles in petroleum larger than 65 Å. Finally, with regard to passive asphaltene tagging, "...it is practically impossible to identify the individual hydrocarbons."[126]

A fair amount of palynological data relating to oil exploration and its various ramifications (little of it representing even an attempt at quantification) has been published during the last decade. Hedberg[129] reviewed some of this work briefly in 1964. Contrary to the opinion held by Sergienko, there is a wide variety of microsolids in petroleum which are greater than 1 micron in size. In fact, the evidence is indisputable for the "...widespread presence of identifiable plant and animal remains in petroleum...";[129] problems do occur, however, when the origin, character, and distribution of these remains are considered. In general, emphasis has been upon the qualitative nature of the spores and pollen in crude oil; few sophisticated techniques have been advanced since Sanders' paper. The only exception to this is a Russian paper published in 1963;[130] this work suggests some of the more common palynological techniques for analyzing crude oils and ground waters. The literature on palynology is perhaps a better source for such techniques. It is good to keep in mind, however, that the selection of appropriate solvents and/or chemical reagents allows the isolation of almost any solid.

More interesting than the work on specific analytical techniques has been that on the geographical distribution of microfossils in crude petroleum.[131, 132, 133, 134] It has been discovered that certain geological ages left distinctive microfossil remains in their crude oils. Chepikov & Medvedeva[135] demonstrated that the crude oil in the European U.S.S.R. is distributed in three very distinct zones: the Volga-Urals region, the pre-Caucasus region, and a transitional region around the Ukraine. Such a general characterization, however, is of little use for tagging crude oils; why it is too difficult to extend this technique to smaller geological zones for this purpose will be discussed in more detail in the following section. Tomor[136] was probably the first investigator to observe this property of crude oils experimentally; his latest paper indicates the possibility of its use for age determinations. Bliznichenko[131] observed "ancient" types of algae in crude petroleums of the West Siberian Lowlands; unfortunately these algae did not correlate with the age of the rock deposits surrounding the oil. Speculation followed. Again no quantitative measurements were possible and the palynological character of the oil in a given deposit was not at all consistent with other facts and/or was not consistently repeatable. In a 1967 paper (Chepikov & Medvedeva)[132] an attempt was made to relate oil and gas migration to the various spores, pollen, tissue, microalgae and microfossils found in them. If entrainment of those materials is assured upon contact with a migrating fluid, this technique makes some sense; however, the indications are once again that the impossibility of quantitative measurement and the migration of the solid materials themselves rule out passive particle tagging. deJersey's[134] work (1966) leads one to the same conclusion; he was able to make some general statements about oil and gas migration and history but no differentiation of similar oils from different deposits. Again there was evidence that crude oils have and still are picking up spores, pollen, microalgae, and microfossils; since such a process would most probably be accelerated in an oil spill, even qualitative determinations would become much more difficult. An example of this is the different character of oil and natural gas from the same petroleum deposit. The work of Horowitz & Langozky[133] in Israel utilized some techniques new to the field, but the results were generally the same as those above. Upper Triassic oils (small spores, 10-20 microns) could be differentiated from Miocene-Pliocene oils (larger spores, 20-80 microns), and contamination of the Triassic oil was indicated. As did Chepikov & Medvedeva,[132, 135] they also noted that pollen migrates quite readily through rock formations; this is especially true when water is present. They were the only research group to notice analytical difficulties due to contamination by asphaltenes and an abundance of pollen and spores. All in all, the palynological studies which have been made over the last 30 years indicate that these techniques are not advanced enough to allow characterization of different lots of crude oil in the general case.

4.3.2.2 Nature of Microsolids: It was necessary in the previous section to mention some of the more general types of particles found naturally in crude oils. This section serves to elaborate briefly on each of these in order to demonstrate that, in the case of a specific particle, differentiation is usually possible. Again, J. McConnell Sanders' study[124] provides the most extensive, published cataloging of the types of particles most often found in crude oils; if the reader is interested in the detail possible on these, he should definitely obtain a copy of this paper.

As might be expected, most of the observed microparticles have been pollen or spores; the papers of Sanders,[124] Hedberg,[129] and Chepikov & Medvedeva[135] indicate, however, that many other materials are also present. The fact is that most investigators do not look for other materials. Besides the spores and pollen ranging from 5 to 100 microns, diatoms are often observed. These small, unicellular algae are present in approximately the same size range, they are readily identifiable and, therefore, present no particular difficulty in microanalysis. Only two types of particles are usually found which have a well defined spherical geometry: pyrites and resins. Even these are often not perfectly spherical and can be identified quite readily (usually by visual techniques). This fact is of importance since carefully controlled particle tagging would most probably involve spheroids of about the same size. Also observed have been foraminifera, acarina, colonies of many protists, antheridia, fungal hyphae, trichomes, etc. The variety is almost endless and, therefore, the possibility of complete quantitative and qualitative analysis is very, very slight. Pieces of tissue abound in crude oil; these may be either plant or animal in origin and are hard to identify in any specific case. Fossilized plant and animal remains are usually found; these often occur as fragments. Regarding the environment, it is not surprising that much partly decomposed vegetable matter is found. Pieces of shells, feathers, hairs, scales, petrified wood, etc., are generally present; they often interfere with analytical techniques. Many of the preceding materials are very fragile and are affected by investigative techniques; besides the variety of materials present, this is the major reason why obtaining meaningful quantitative data is so difficult. One's attitude to these materials, in this respect, should be one of elimination rather than consideration.

4.3.2.3 Techniques: Practically, the optical limit for microscopic analysis is about 0.5 microns.[137] Fine resolution is obtained only for particles quite a bit larger than this; generally it is preferred to work at or over 5 microns. These larger particles may be studied with standard laboratory microscopes, and their fine structure can be resolved down to about 0.2 microns. Palynology has a wealth of techniques for the microscopic examination of the solids in crude petroleum, but little to offer over and above the methods used by Sanders in 1937.

Brown's book[138] contains a fairly extensive review of palynological methods. However, the technique he presents for analyzing crude oil (p. 115, Sittler's method) is quite harsh; that is, much particle destruction is assured. For instance, (1) HF treatment, (2) boiling in KOH, and (3) acetolysis are only three of the suggested steps. It is not surprising that analysis such as this often indicates the presence of only very small amounts of particulate material (e.g., residue from the Rancho La Brea tar pits and Uvalde asphalt). In contrast, Sanders' methods (and those workers who have followed his lead) are much less destructive and do not appear to yield inferior results. The most valuable advice contained in Brown's treatise is that particulate-specific solvents and reagents should be found and used when much solid matter must be processed; this is especially relevant for active tagging since small amounts of the tagged material may be in the presence of (possibly) large amounts of other solids. Another specific technique is preliminary centrifugation rather than filtration; with sufficient time for treatment, this is much less liable to promote the loss of important microsolids. Practically, centrifugation limits the amount of oil which may be conveniently processed; but then, so does microfiltration.

Sanders' use of organic wash liquids is the most suitable for the general examination of the solid residue from crude petroleum. As previously mentioned, centrifugation would probably be more successful than Sanders' filtration in preconcentrating microsolids. More exotic methods than these are indeed available (see Miziuke 1965),[139] but would add little to the process being considered here. The use of the usual wash liquids ($n\text{-}C_5H_{12}$, CCl_4, CS_2) would most probably be sufficient; however, development of an active tagging scheme would involve finding a specific maceration technique anyway.

A scheme for microscopic examination, based on the works mentioned previously, is outlined below:

a. Approximately one liter of retrieved, spilled oil is cut with a light organic liquid (e.g., n-pentane) to reduce its viscosity.

b. The resulting suspension is centrifuged (or filtered) to isolate the solids.

c. After decanting the oil phase, the solids are resuspended in a light organic liquid and recentrifuged; this is done about 5 times.

d. The particles are then filtered and trapped on a Millipore filter.

e. Depending upon the nature of the tagging particles, the solids are then washed with appropriate liquids (e.g., CCl_4, CS_2, H_2O, KOH, CH_3CH_2OH, HNO_3) to remove background particles and clean the isolated solids.

f. With a hypodermic syringe, a sample of the particles, suspended in a highly volatile liquid (e.g., acetone) is transferred to a microscope slide.

g. Under the microscope, the relevant tagging particles are isolated further, and any necessary preliminary tests are made on them.

h. The now completely isolated particles may be transferred from the slide for more extensive analysis (e.g., to a sedimentometer for density determination, to a standardized mount for size measurement, or to a microspectrofluorometer for spectrographic characterization).

4.3.3 Production of Microparticles

The production of finely divided solids is a field for study in its own right; for instance, the minerals and ceramics industries have long been interested in and have utilized fine grinding to obtain micro-sized particles. Their problems are unique, however, in that they are concerned with the processing of quite large quantities of relatively heterogeneous materials. Conversely, the operation envisioned here involves only relatively small amounts of what is hoped are fairly homogeneous solids; this homogeneity extends beyond the chemical constituents of the particles to both their size and shape. The literature which addresses itself to these sorts of criteria is not very extensive; however, the indications are that with available technology the problems are soluble (subject, of course, to the results of reasonable engineering studies). Although particles of widely varying sizes and shapes but of reasonably similar chemical composition can be obtained, only one shape is convenient for the production of large numbers of "completely characterized" particles: the spheroid. Given that homogeneous solid material is obtained by (1) solidification of a liquid melt, (2) coprecipitation from solution, (3) efficient mixing and sintering of suitable solids, or (4) deposition from a vapor phase, it has been found that almost any such material may then be spheroidized.

In addition to characterization and technological feasibility, microspheroids are advantageous for several other reasons: (1) Their small surface area per unit volume and lack of areas of large surface curvature make them less susceptible to chemical reactions; (2) these same qualities make it more unlikely that they will clog or impact upon passage through small apertures, or adhere to interfaces; and (3) microspheroids are much more easily and reliably sized (e.g., by sieving, sedimentation, and microscopic methods) than any others. The flowability of microspheroids makes them ideal for unit operations where mixing is necessarily of importance; flowability is obviously important where trace solids are to be added to a very large amount of liquid. The above points also apply to simplifying the preconcentration and isolation required in any analysis of suspensoids. Finally, small particles (10-50 microns) are not rare in nature; but very smooth microspheres of this size are much less common.

4.3.3.1 Techniques: There is a fair amount of literature on the production of microspheres. Using spheres in experimental studies is often desirable since much of the theoretical work on particulates has involved assuming such a shape; for instance, think of the usual approach in fluid mechanics for studying the velocity distribution around a solid in a moving fluid (i.e., Stokes' analysis), or the basic approach to the reaction of solids in physical chemistry. Much of the material presented by Allen[140] is based on a spherical geometry, although it is applied to similar, nonspherical particles by introducing proportionality constants. Due to their having the minimum surface-energy configuration, spheres (especially small ones) may be formed quite readily; in nature, however, interactions with other particles and the presence of directional forces often prevent their formation. The most common microspheroidizational process is liquefaction of a particle followed by solidification in a dilute, slowly moving, gaseous "suspension." Other techniques have been used: Lucite spheres are produced commercially by tabling; deposition from a liquid solution has been tried for certain resins; and by mechanical action, the polishing compounds used in ball mills may be used to produce ceramic or glass spheres.

In 1934 Sklarew[141] proposed what was probably the first system for making glass microspheres, which are now commercially available in a few types of glass. His apparatus was cumbersome and made a significant number of nonspherical particles. Since it is difficult to separate micron-sized particles according to shape, this method was generally rejected. Sollner[142] modified Sklarew's approach and came up with a simple system which produced essentially perfect spheres among all of the thousands which he observed microscopically. These spheres were 15 to 50 microns in diameter; the smaller size is set, practically, by the limit of the microscope he used and by his preliminary sizing procedure for the rough particles. Sollner's paper contains a sketch of his apparatus; it is delightfully simple. Oxygen is passed through a fluidized bed of the sized, rough particles which are to be spheroidized; particles are entrained and pass into a simple glass torch. The smooth glass torch is used to prevent unnecessary particle abrasion. If soft glass is used, the flame may be oxygen-methane; for Pyrex or Kimax, an oxygen-hydrogen flame is necessary. The particles are trapped in a pool of water toward which the flame is directed. Besides being almost entirely spherical, the microsolids treated in this way were found to be strain free, as was shown by analysis with Nicol prisms. Freedom from strain is highly desirable since it lessens the chances for further particle degradation and reaction and reduces the possibility of spectrographic anomalies due to structural distortions.

Bloomquist & Clark (1940)[143] modified Sollner's experiments by using a standard "blast lamp" torch and a stovepipe-funnel-filterbag collection system. They produced the rough fine particles by wet-grinding Pyrex in a ball mill for several hours and then sized them with 12 to 15 decantations at 5-minute settling times. The spheres which resulted from this procedure were remarkably good (see the photomicrograph in their paper). For five nominal sizes of 25 microns and less, they made statistical analyses; about 98% of the particles were found to be spheres, and 90% of these were ±2 microns of the nominal size. This statistical size distribution can be significantly improved by decantation after spheroidization, if necessary. These experiments were run with very inefficient, batch processes: About 300 grams of closely sized microspheres (in five sizes) were produced in 10 days. Yet, as shown and discussed in more detail later, this is enough to tag about 500,000 tons of crude oil! It is also what amounts to a custom synthesis.

Laan & Nicholls[144] constructed a simple apparatus for making 10- to 100-micron spheres of low-melting metals. It amounts to nothing more than a small, modified shot tower operated at 10 to 40 psig in an inert nitrogen atmosphere. Liquid metal is drained from a chamber and passed through a 0.1-inch-diameter nozzle. The metal solidifies in a 6-foot free-fall region; a rough separation of spherical and nonspherical particles is achieved by infall on a slightly tilted collection plate.

Potter[145] describes an apparatus suitable for higher-melting materials; liquefaction is achieved in the plasma of a direct current-arc column. Better grading is achieved when previously sized particulates are used; both shot tower and wire sputtering suffer in this respect. Helium is used as an inert carrier, and again free fall permits solidification. The primary advantages of plasma spheroidizing are (1) large throughput rates (as high as 20 pounds per hour) and (2) adaptability to processing a wide range of materials: Over a very wide range of melting points, plasma-jet spheroidizing is successful. A plasma-jet flame reaches temperatures of 50,000°F; therefore, fine powders with moderate melting points (e.g., Pyrex) are virtually 100% spheroidized. An example of the efficiency of this process is found in the treatment of zirconia (melting point, 2700°C); 80 x 120 mesh (about 150 microns) particles are 95 to 99% melted and 85% spheroidized. The Thermal Dynamics Corporation uses such a process.[146] Microballoons of 25 to 300 microns are produced commercially[147] from a number of glasses and organics; the process involves passing a volatile solvent solution of a filming material through a spray-drying tower. A suitable vapor-generating material must also be in solution or spheroids form; these spheroids represent a possible analytical interference when similar materials are used for tagging crude oils—note that microballoons are widely used for evaporation control in storage tanks. Careful microscopic examination should resolve this problem, however.

4.3.3.2 Materials: Of course, soft glass is the most common material from which microspheres are made. Such glass may be "doped" with a wide range of metallic salts, and it usually has some present as impurities. Microanalysis for such impurities allows a tremendous amount of information to be obtained from a single microsphere. Similar doping capabilities exist for the solids which are mentioned below. As previously mentioned, the hard glasses, e.g., Pyrex, may also be spheroidized. Plasma techniques allow the processing of most metals and ceramics. Zirconia has been mentioned above; alumina, many oxides, nitrides, and carbides have also been made into microspheres. Laan and Nicholls' apparatus[144] is suitable for spheroidizing materials such as lead, zinc, and cadmium. With regard to the lower density materials which may be more suitable for oil tagging, spray drying, as well as the other techniques, may be used. This process has been used to make spheres of glass, cellulose, starches, polystyrene, phenolic resins, and many other organic compounds. Treatment of homogeneous solutions by spray drying would permit simultaneous doping and formation of microspheres.

One concludes there is no problem with microsphere production. It can be done on a laboratory scale using standard techniques; doping is relatively straightforward and so is handling. For the application being considered here, sufficient production capacity is assured. Once the process has been developed, technicians would be able to do most of the work involved.

4.3.3.3 Addition to Petroleum: The metering of small amounts of liquids has been developed by the chemical, pharmaceutical, and processing industries. For particles of the size which we are considering, the same techniques will suffice. The problems of contamination and analytical control are of primary importance. Both the metering system and the equipment used in particle production and analysis should be easily cleaned or inexpensive enough to be disposable. The simpler production equipment is both; only the modified shot tower and the plasma-jet apparatus would involve tedious, but necessary, cleaning procedures; the spray-drying column is easily cleaned since it is, in essence, a liquid processing unit. In no case need the particles and/or the initial process materials make contact with the analytical equipment; therefore, cleaning is not a problem.

Addition of a tracer material to petroleum involves two similar and related criteria: First, the trace material should be in a homogeneous phase, and, second, this carrier phase should be injected uniformly into the petroleum so that the resulting tagged dispersion (or solution) is also uniform. There is ample evidence that relatively stable dispersions of particles in a petroleum-based liquid are easily produced. It is important that this stability be maintained when the carrier fluid is injected into the petroleum. Khomikovskii & Rehbinder[148] found that maximum dispersion stability correlates with maximum surfactant adsorption for pigments in oil. In crude oil, enough surfactants are usually present to assure stability (at least for the dilute suspensions we are considering); in refined petroleum products, it may be necessary to select the particle material with great care so that the appropriate surface properties pertain (i.e., relative hydrophobicity and oleophilicity). Highly polar materials (e.g., ionic salts) actually stabilize suspensions when the particles are larger than about 1 micron (Koelmans);[149] the only important exceptions are metal sols, which are, however, stabilized by metallo-organic molecules (e.g., chelates). According to Koelmans, ". . . a system is stable when a crossing of the potential barrier between the particles by thermal motion alone is very improbable"; this potential barrier is about 15 kT for a modestly charged double-layer and is much greater than the usual thermal energies (about 1 kT). This energy difference also applies to particles approaching an interface: Thermal energies cannot overcome the surface potential barrier. Very concentrated suspensions (20 to 90 wt %) may be stabilized by adding small quantities of dissimilar particles;[150] this stabilization technique may be of value in prescribing carrier suspensions.

Once a stable carrier suspension has been produced, it can be metered into petroleum without further problems. Many metering pumps are available at nominal cost; some of these (through mechanical action on a disposable diaphragm, bladder, or flexible tube) do not even contact the metered fluid. Since the volume of the metered suspension may be increased almost at will, pump capacities are not of special importance.

In conclusion, sufficiently stable particle suspensions can be produced and then successfully metered into petroleum which is to be tagged; since this latter step represents a very large dilution, the resulting suspension is expected to be very stable.

4.3.4 Retrieval from Spills: Preconcentration

Although difficult, it is possible to collect very large samples of spilled oil; however, the analytical techniques described in the previous sections involve, ideally, relatively small amounts (i.e., 200 to 1000 ml). Such volumes of crude oil and liquids, which have long been exposed to air, contain fairly high concentrations of particulates (Krueger, pp. 622-633).[137] Reference to Horowitz & Langozky[133] allows selection of a typical tagging concentration: A few hundred particles in a few hundred milliliters of oil are easily detectable. Therefore, we may specify 1000 particles per liter. As an example, consider medium-density particles (1.0 gm/cc) in a medium-density suspension (1.0 gm/cc) and calculate the total mass of particles M_{total} (10 microns in diameter) in 100,000 metric tons of suspension (approximately the load in a tanker):

$$M_{total} = \frac{100{,}000 \text{x} 10^3 \text{Kg}}{1.0 \text{Kg}/l} \text{ x } (1000/l) \text{ x } \left[1.0 \text{ gm/cc x } (4\pi/3)(5\text{x}10^{-4}\text{cm})^3 \right]$$

A one-liter sample of oil ($\approx$ 50 gm) with only 5% the average number of particles (i.e., 50 particles) would still be amenable to analysis. Since 10- to 50-micron particles are uniformly and stably dispersible in oil, there is no problem in obtaining a well-tagged sample. Probably the most critical point in sample retrieval is that oil should be sampled from several places; these samples should then be mixed uniformly and the analytical sample taken from this blend. Dispersed water should also be processed in the preconcentration stage because some particles may be found in the water phase of oil emulsions; either filtration or centrifugation will successfully isolate these particles. It may be desirable to homogenize oil-water dispersions (say with lanolin) to facilitate separation.

4.3.5 Particle Characterization

After tagged particles have been isolated from an oil spill, many identification procedures are possible. These range from simple qualitative to more complex quantitative schemes. Visual identification and counting are the most common palynological methods; as mentioned previously, these methods are, however, subject to a number of errors (e.g., operator bias). Visual recognition of particle shape is definitely qualitative; therefore, the shape should be standardized and easily recognized (i.e., we consider spherical particles). Since particle shape is set in this manner, preconcentration and/or isolation are well-defined unit operations. When the spheroids have been isolated, analysis of the character of individual particles may begin; physical and/or chemical techniques may be used.

For a spheroid, size measurement presents little or no problem; standard microscopic gratings which allow accurate and convenient comparative measurements are available (McCrone et al.[151]) Particle diameters down to several microns may be determined in this manner. It is more difficult, but possible using standard techniques, to measure the density of microspheres (Blanchard).[152] If we consider particle sizes of from 10 to 50 microns with an error of ±2.0 microns for a given size, there are at least 11 distinct and well-defined sizes. For density, with a range 0.9 to 1.50 gm/cc and an error of ±2%, we have, again, at least 11 possible characterizations. The product of the numbers of these two properties gives 121 distinct particle characterizations. In many cases this would be sufficient for tagging fluids or solids, but the large number of shipments of petroleum makes it necessary to expand the characterization. Ultramicroanalytical methods are widely available (see Kirk[153] or Meinke[154]). Microchemical techniques for a single particle are also available from standard microscopy. Particles which contain trace amounts of chemically detectable materials may be characterized either qualitatively or quantitatively. For instance, a standard series of microtests could easily determine whether or not 20 or so identifiable trace chemicals are present. With a very simple binary code, this number of trace chemicals would represent 2^{20} (1,048,576) possible particle characterizations. It is important to emphasize that this tagging scheme is simple to execute and that the number of possible characterizations presented above is a conservative one. Since these chemical techniques are well known, no further elaboration is necessary.

A fascinating possibility is the use of spectrographic techniques. These may be qualitative (Sventitskii)[155] or semiquantitative (Harvey)[156] or quantitative (Hercules).[157] Furthermore, spectroscopy may be used to analyze particulate assemblies or single particles. Regarding the former, standard microanalytical techniques apply directly; in fact, for particles less than 5 microns in diameter, suspensions may be treated spectrophotometrically as homogeneous fluids (Lebedev).[158]

In practice particulate assemblies may also be solubilized, and analysis run on the resulting solution. In the treatment of either a suspension or a solution, a very large number of trace materials may be detected; for example, Sventitskii used a steeloscope and was able to detect nine elements at the concentrations given in the table below.

Element	Detectable Concentration (weight percent)
Cr	0.01 to 0.10
Mn	0.02 to 0.15
Mo	0.05 to 2.0
W	1.0 to 18.0
Va	0.2 to 2.5
Ni	0.03 to 0.3
Cu	0.05 to 0.6
Mg	0.02 to 0.12
Zr	0.1 to 1.0

The detectable concentrations given above are for strictly visual observations. With photographic assistance, Sventitskii[155] was able to detect 17 elements at 0.1 or less weight percent (p. 240); obviously, although his techniques were qualitative, a degree of visual quantification was possible. Note that the detection of 10 elements at four concentration levels yields the same number of characterizations as for the binary system presented above.

Some of the preceding work was semiquantitative; Harvey's entire book[156] considers experimental techniques of this sort. It is best, therefore, to consider quantitative analyses directly. Since a very specific detection scheme is necessary, spectroscopy is a logical choice. In fact, a unique spectrographic trace for either a group of particles or a single particle gives rise to the possibility of a general "fingerprint" or trace for any tagging material. This has two effects: (1) Although the technique is quantitative, it is used qualitatively since only the specific particles need be identified. (2) By adding appropriate chemicals to the particle matrix, spectrographic traces may be "custom made." Since these traces are then very specific, the possible number is almost limitless. For example (although one should note that what follows is too restrictive), given 20 distinguishable spectrographic peaks (at different wavelengths) which may be detected at five different intensity levels, we find that there are 5^{20} or about 10^{14} possible characterizations. This number is, to say the least, sufficient.

4.3.6 Costs

The materials' cost for particle tagging should be quite small. The matrix of the particles will probably be a quite common plastic or glass: cost, a few cents to a few dollars per pound. The trace materials imbedded in this matrix would cost about the same but would be used in almost negligible quantities. More expense would be involved for the capital equipment to do the necessary tasks. For instance, laboratory apparatus to produce the microparticles would run in the neighborhood of $5000. A microspectrofluorimeter, with a lens system for single-particle measurements, might cost $30,000; note that spectrographic analyses of the desired type may also be purchased commercially for about $50 per sample. High quality microscopic equipment would be an absolute necessity; it is available for from $4000 to $20,000 (McCrone).[151] A metering system for the tracer fluid would probably cost $20,000 to $100,000; a single metering pump is inexpensive (about $200), but a fairly large number would be necessary in a practical distribution system. Additional capital costs would include laboratory and office facilities, field-analytical equipment, etc.

As in many projects of this sort, the cost of labor would be very important. Considering that a large amount of petroleum might have to be tagged, five laboratory workers, 50 field workers, and managerial and office help would be necessary; running costs for this labor would be 3/4 to 1 million dollars per year. This, of course, is predicated on all the work being done by one specialized group.

We should note that the above cost breakdown is for complete fabrication and operation of a petroleum tagging center. These costs are not applicable to feasibility studies and the like. Since much of the equipment is available, it could be modified for a limited study; personnel who are familar with the necessary analytical methods are also available. A development and demonstration study seems very attractive, and could be conducted at nominal cost. It should be remembered that the results of such a study would be applicable to work much divorced from the tagging of petroleum (e.g., tagging solid wastes and studying particle transport in rivers).

4.3.7 Summary and Conclusions

It is hoped that the preceding sections have given a reasonable picture of the possibilities of both active and passive particle tagging (insoluble tags). Besides its obvious application to the tagging of crude oils, active particle-tagging has many other possibilities: tagging and the concomitant study of solid air-pollutants, labeling pharmaceuticals, trace analyses in systems with multi-effect mixing phenomena, and the growing study of microparticulate systems in general. Since the possibility of a large number of easily produced and/or procured microsolids has already been illustrated, applications using them are now enhanced considerably.

For the particular problem being considered in this report, the conclusions which follow have been reached. First, generally:

- Passive tagging with microsolids is not at all a realistic approach.

- Active particle tagging is.

Passive particle tagging must be rejected for the following reasons:

a. Other than for very general characteristics, it is difficult to attach specific significance to the particles found in crude petroleum; that is, the element of control is severely lacking.

b. Many of the solids which occur naturally in crudes are extremely fragile; the technique of analysis, therefore, bears much too heavily on their detection.

c. Most of the particles found in isolated crude petroleum occur in the ambient; therefore, in the case of a spill (i.e., exposure) they will be picked up. This will render almost meaningless any identification based on the distribution of particulates in the original crude.

d. Identification of a particular oil involves a statistical analysis with an error factor(s) very difficult both to identify and quantify (especially with spillage, transport, exposure, varied handling techniques, etc.); in a single case this problem is a tough one—for multiple spills it would be intractable.

On the other hand, active particle-tagging should be carefully considered for the following reasons:

a. Well-characterized microparticles may be produced from a very wide variety of materials (e.g., ceramics, glasses, plastics, metals); these materials are available from a fraction of a cent to $1000 per pound (for a rare metal).

b. Micron sized particles can be injected into a tanker (or the oil as it is either transported or loaded) in gram quantities or less, depending on the detection technique; they will not affect the properties of a crude oil as far as either producers or consumers are concerned (for particles of the size being considered here, injection into many petroleum products would not be harmful).

c. Depending on how detailed the microanalysis is, the characterization may be as elaborate as necessary (e.g., in principle, microspectrofluorimetry would allow a "fingerprint" of a single, 20-micron spheroid!).

d. If the microanalysis is quite detailed, multiple oil spills present no particular problem.

e. The production of microspheres is already developed technically.

f. The necessary analysis techniques appear to be available; these include preconcentration, microscopic observation and minipulation, and quantitative measurement.

Certain problems do arise with respect to this technique, however:

a. Spheroidal particles are found naturally, usually as resins and pyrites. Glass microspheres may also be present when the crude oil has been stored with microballoon evaporation-control.

b. Generally, the smaller the amount of the desired trace material, the larger the spillage sample which must be analyzed.

It is expected that the former may be resolved by careful visual observations during preconcentration. Careful selection of tagging criteria should eliminate the latter.

The exact methods for analysis depend on many factors; hardly the least of these is the development of such a particle tagging program itself. A thumbnail sketch of what, at this time, appears to be a reasonable procedure follows:

a. Microspheres of about 10 microns diameter would be produced by spheroidizing an appropriate, finely ground and sized solid.

b. These particles would be characterized in preliminary tests to the necessary degree.

c. They would then be metered into the specified petroleum (preferably as it passes through a pipeline or as it is pumped into a tanker). In order to have, on the average, 10^3 particles per liter of oil, only about 5×10^{-4} gram of particulates needs to be added to each ton of oil; this amounts to 50 grams for a 100,000-ton tanker.

d. Upon spillage, a representative sample would then be taken from the slick.

e. The particles in about a liter of spilled crude would then be preconcentrated as follows: (1) centrifuging and washing with a light hydrocarbon, (2) washing with more digestive liquids (perhaps acids and bases), (3) a terminal filtration and wash on a Millipore filter, and (4) transfer of the solids to appropriate microscopic mounts.

f. The same analytical steps would be run as in step b. to identify the particles. These tests could be visual microscopic (e.g., size and/or shape, color, fluorescence, phosphorescence), or microanalytic (e.g., density, hardness, trace analysis), or microspectrometric (e.g., light absorption, fluorimetry, reflectance). Microspectrofluorimetry could provide a characteristic spectrograph of just one or a number of particles; such a trace would, indeed, be a "fingerprint."

g. The data obtained from the particles in the spilled oil would be compared with that of the preliminary tests (which should be properly cataloged), thereby identifying the source of the spilled oil.

h. In the case of a multiple spill, the individual offenders could be identified quite readily. Determining the portion of a spill which each is responsible for would, however, involve characterizing a larger, representative sample of microparticles; based on the number density of each type particle, proportional liabilities could then be estimated.

It is unfortunate that a technique such as that above has not yet been developed; the tool that such a scheme represents may prove to be of monumental importance. The necessary technology is available; all that remains is to put the system together and develop it properly. The fact that such has not been done in the field of petroleum technology reflects only the lack of knowledge of and interest in particulate systems; this can also be observed in many other fields of study. This situation is, however, changing quite rapidly. Perhaps, due to the study proposed here, interest will be revived in the nature of particulates in crude oil. Anyhow, there is no doubt that petroleum can be simply, economically, and effectively tagged with microspheres. Such a study will open up a new area in pollution technology and technology in general.

4.4 Radiochemical Tagging

There are two general alternatives in radiochemical tagging: (1) addition of radioactive isotopes to the potential pollutant, and (2) addition of material that lends itself to neutron-activation analysis. While both alternatives have been used in water-pollution studies, the use of radioactive isotopes has been limited (for excellent reasons) to a very special type of study. Neutron-activation analysis, on the other hand, has been widely used.

Radioactive isotopes may be used advantageously when the product to be tagged is not stored. Harremonës,[168] for example, has routinely used one curie of bromine-82 (as ammonium bromide) in tracer experiments to select sites for sewage-disposal plants; these methods are apparently standard in Denmark, and are used in experiments

> before selection of the site for future sewage disposal from industries and municipalities.... The movement and dispersion of the tracer is recorded by a ... boat sailing in and out of the cloud of radioactivity.... Tracer injections at different sites permit a selection of the most economical site and of the required purification of the sewage.[168]

Guizerix[169] has reviewed the use of radioactive tracers (principally bromine-82 and iodine-131) in water-pollution research. In all the uses he reports, the radioisotopes are released instantaneously or regularly (at short intervals) and measured regularly. Very "hot" radioisotopes are never added to a product that will be stored, for the simple reason that the isotopes rapidly decay. The half-life of bromine-82, for example, is approximately 40 hours, and the half-life of iodine-131 is about 8 days. Indeed, the rapidly-decaying isotopes that have high disintegration energies are used as tracers precisely because they are detectable in very small quantities. However, even when such "soft" and long-lived isotopes as tritium are used as tracers, the experimenter must still comply with strict governmental regulations. Consequently, even tritium (see, for example, Guinn[170] and Anguenot[171]) is almost always used in carefully controlled laboratory studies, and every effort is made to ensure that the isotope does not escape into the air or the water: For, if a rapidly decaying isotope escapes, its danger will be intense but short-lived; but if a slowly decaying isotope escapes, the danger will be long-lived.

Ideally a radioactive tag should have a half-life of 90 days, be readily available, be low in cost, and easily detected. To be effective as a tagging system there should be a minimum of 30 radioactive tags all of whose half-life is close together.

Tags with short half-lives will not remain detectable during long voyages. Furthermore, freshly activated tags would have to be furnished to the tagging groups quite often. Tags which do decay, however, are useful because old tags disappear and the tagging system noise is decreased. For these reasons the ideal half-life would be over 60 days.

Long half-life isotopes present a serious problem because of their slow disintegration rates. For the same counting rates far higher concentrations of long half-life isotopes would be added to the oil. When the oil is subsequently burned as a fuel the radioactive material would get into the air and into the food chain. This would be a very touchy political problem not to speak of the medical implications.

With an ideal half-life of 90 days and the requirement that all tagging isotopes used have a half-life close together, it is instructive to note that there are a total of 11 isotopes with half-lives between 90 and 120 days and 18 with half-lives between 90 and 180 days. In fact, there are only 10 gamma emitting isotopes with half-lives between 60-180 days, six between 180-365, and 33 with over 365 days (gamma is the easiest to detect). When the energy spectrum of the gamma emitters is examined for isotopes over 0.3 MEV there are only 4, 2, and 22.

Radioactive tagging is unfeasible because there are not enough tags of the right half-life, and if one goes to long half-life tags, the problem of air pollution by radioactive materials becomes both a political and medical issue.

To circumvent these difficulties and dangers, neutron activation is often used. Neutron activation is (in a sense) the mirror image of radioisotope tracing: Instead of converting an element into a radioactive isotope before using it as a tracer, the element is made radioactive only after the inert tracer has been collected and prepared for analysis. Chatters & Peterson,[172] who used neutron activation to study polution from a wood-pulp mill, have summarized the advantages of neutron activation over radioisotope tracing.

> This method eliminates those problems usually associated with the handling of isotopes in [paper] mill. It also obviates the necessity of having to comply with local, state of federal codes-of-regulation [sic] relating to the use of radioisotopes within a mill or their disposal into public waterways.

Neutron-activation analysis is now a widely used analytical technique; it is often used in the petroleum industry to provide rapid and sensitive elemental analyses of refi[illegible] product consumption, and catalyst poisoning.[173] Neutron activation (using small accelerators) is routinely used for determining such elements as O, V, Mn, As, Cl, Br, I, Si, Al, and Na in concentrations of 0.001%; with more powerful equipment, the level of detection can be made some 10,000 times more sensitive.

However, neutron activation is only one analytical technique among many; it is no analytical panacea. In some cases other techniques (such as chromatography and spectroscopy) are more sensitive, or more accurate, or less subject to interference. Each case must be decided on its own merits. Insisting on neutron activation would be as pointless as insisting on any other analytical technique; all such arguments beg the question, which is: What inexpensive, stable, active tag is suitable for identifying oil spills? Having found suitable active tags, it is a relatively small matter to choose the most powerful and sensitive method for identifying them.

SECTION V

IMPLEMENTATION OF THE TAGGING SYSTEM

Up to this point the feasibility of using additives to tag oil has been discussed. It has been concluded that passive tagging is ineffective, but that active tagging is both practical and economical. Discussed below are the mechanics and coding of tagging. To effectively tag, a series of steps must be taken, such as adding the tagging material to the oil, canceling the tag, checking the quality of the tags in the material, as well as keeping the codes as flexible as possible. The purpose of tagging is to use a series of unique codes that are specific and unique for each legal jurisdiction.

5.1 Marking and Identifying Oil Shipments

The mechanics of adding tagging material include a series of steps. Only five (jurisdictional taggings) are presented here: oil (1) entering a tank farm, (2) entering a tanker, (3) being received at a refinery, (4) entering another tanker, and (5) arriving at a user's tank farm. Many of the casual spills are believed to occur at a transfer point. Thus, tagging oil in these jurisdictions will cover a majority of the spills.

The tagging material will be added by metered pumps ahead of the main pumps as the oil is on-loaded or off-loaded from a tanker. The tagging fluid for the refinery will be kept by the refinery and that for the tanker will be carried by the tanker. Each ship will have its own code and will maintain cognizance over the coding material. Each time oil is loaded on a tanker, the tanker's coding material will be added to the cargo. Samples will be taken on the downstream side of the tagging point for the "record" and for "quality control." Periodically, grab samples from tank farms and from tankers will be analyzed to determine the code present, and to ensure that the material is tagged as required.

5.1.1 Oil Tagging at Transfer Points

Because it is believed that the majority of the casual oil spills occur at transfer points or from tankers, the initially recommended coding system should start by tagging all oil entering into shipper's tank farm. Thus, all oil in the tank farm's jurisdiction will have its own unique code and any oil spilled on the waters from this jurisdiction, for whatever reason, can be attributed to the tank farm. When a tanker is to load, the harbormaster will obtain from the tanker captain the coding solution and insert it into a special metering pump ahead of the main loading pump. As the oil is pumped into the tanker, it will be tagged with the tanker's code and will be in the tanker's jurisdiction. Any oil spilled downstream of the pumps will be considered in the jurisdiction of the tanker. When the tanker departs, any oil on the water with the tanker code will be in the tanker's jurisdiction. As the ships ply the high seas, any housekeeping adjustments made, causing a spill, will have the tanker's code, or license plate, in the oil. Should this oil cause damage or be recovered subsequently from the ocean's surface, the tanker's jurisdiction over the oil and responsibility for damage can readily be established. Upon entering the harbor and off-loading into the tank farm, which in this case may belong to a user or refinery, the tank farm's coding material would be put in by a meter pump upstream of the main off-loading pump on the tanker. This new code added to the oil will effectively cancel the tanker's jurisdiction and establish the tank farm jurisdiction.

5.1.2 Determining Jurisdiction

If a spill should occur during on- or off-loading, both the tanker code and the tank farm code will be in the oil. Both parties will have observers, and responsibility for the incident should be readily affixed. The spill will be clearly tagged with the time and date confirmed.

5.1.3 Mechanism of Adding Tags

The actual mechanism of adding the tag material is quite simple. Using existing (or slightly modified existing) metering pumps, small quantities of the tagging element in a carrier fluid will be pumped into the oil stream ahead of the main pump. The turbulence of the pump and the subsequent turbulence resulting from the pressure drop will mix the tagging material throughout the stream. As one or more minute streams of carefully metered tagging fluid are added to the stream, the shearing action of the pump and the other turbulence will mix it thoroughly. Subsequent movement of the fluid and normal diffusion will continue to spread the tags throughout the oil.

5.1.4 Tag Control

Each jurisdiction will carry its own tagging fluid and will be responsible for safeguarding it. Thus, the shore installations will be responsible for furnishing to the harbormaster the necessary tagging fluid when material enters their jurisdiction and, in like manner, the captain of the ship will give the harbormaster his code at the time of on-loading material. This makes it very unlikely that any false tagging can occur. Since the codes even in the early part of this program will be less than simple, it is not anticipated that counterfeit tagging material can be devised. Furthermore, the problem of canceling (or confusing codes) by adding material to slicks is unlikely due to the difficulty of mixing the coded material into an extant slick.

Freshly tagged material, undergoing a jurisdictional change, will be sampled routinely and the sample stored for future reference. In case of a slick where a question arises, the sample could be analyzed for comparison. Furthermore, the sample can be routinely analyzed to determine if the tagging material is being properly added to the oil. If abnormalities occur in the system, they can be detected in the sample and in the oil.

It is also anticipated that samples will be "grabbed" periodically from the tankers' or the tank farms' jurisdictions to check the efficacy of the tagging. In the beginning, these will be used more for quality control of the system and for detecting its effectiveness, and later for checking the system's life. It will be more or less a legal check to ensure that the oil is being tagged properly.

It is believed that the initiation of the system, as well as the operation of it, will be done best by one jurisdiction to minimize code confusion and maximize information. It is further anticipated that there will be unique codes for each jurisdiction, and the codes will be canceled by subsequent addition of tagging material which cancels the former one. Furthermore, dilution in a tank farm is believed to significantly change the concentration and profile of the tag material.

5.2 Codes

For tagging oil there are two classes of codes: license plate code and profile code. In the license plate code, a simple unique tag is added for each jurisdiction, while, in the profile code, a dominant profile of nonunique tags which mark the jurisdiction is added. Both have their advantages and disadvantages and both are practical.

5.2.1 License Plate System

In the license plate system, a unique chemical or unique particle tag would be added. While the number of unique chemical tags is certainly adequate and readily analyzable, particles are probably better in this system because they can be concocted in almost an infinite variety of mixtures and made quite pure. In the license plate system, each tanker would have its own special material to uniquely identify that tanker.

In any working code, there would also be other redundant information. Such information would indicate that the oil had been carried in a tanker or that it at one time had been in the jurisdiction of a specific company's tank farm. In all probability, there would be other bookkeeping information in the coded material, such as dating information, coded batch information, and perhaps experimental coded material, for expansion of the system. However, the unique jurisdictional tag would be present in the oil and, in case of a spill, the presence of this tag would "state" the responsible jurisdiction. The examples following this discussion present the methods of establishing jurisdiction.

5.2.2 Profile System

In the profile codes, a series of analyzable particles or chemical tags is added. Probably a hundred of these tags would constitute the entire system and the actual profile of the material would become quite important. This system is more amenable to chemical tag and is more easily initiated by oil companies with their extensive knowledge of trace organic analysis. However, for a large system, it is the inferior method because much information will be available as to who are the likely culprits. Thus, a quick analysis of the slick for the likely candidates will not be possible and analytical costs will be too high. Furthermore, in complex repeated tagging, the profile differences become less distinguishable. Profile codes require not only the detection of the presence of a code but also the quantity present.

Particulate and chemical tagging can be interspersed without any interaction. Added quantities of a particular tag will be on the order of one part in 10^9 to 10^{11}. Since tags will remain in the oil, being specifically designed to do so, questions of toxicity and effect on final users' needs should not arise because of extremely low concentration. In all probability, any material selected as the tag will be no more toxic that the lighter ends of crude oil itself. The material chosen will have an optimum combination of ease of detection, cost, and compatibility.

5.2.3 Coding Examples

Examples are included in this section to delineate the actual tagging that will be done and the characteristics of the codes as they occur in various jurisdictions. Two examples are given for the license plate tag, and a number of examples are given for the profile tag. The oil in the examples is considered to originate at an oil field and be shipped to a tank farm where it is originally coded. Subsequently, the oil is loaded onto tankers and shipped to a refinery, reloaded onto tankers, and shipped to a final user, which might be a bunkering station. The final user is considered to have a tank farm. Therefore, the oil is tagged at the initial well tank farm, when it goes into the tanker, when it goes into the refinery tank farm, when it is on-loaded into the second tanker, and when it is finally off-loaded into the user's tank farm—five taggings. In the example, the actual code is traced through each of these steps with redundant information being added at each step to further assist in its analysis.

For a "license plate" system, a unique material is added at the jurisdiction. As the oil moves from one jurisdiction to another (for example, as it is off-loaded from a tanker into a tank farm), it is usually diluted or mixed with other oil in the tank. This plays an important role because the last tagging code is in full strength. For example, an oil from a well tank farm source, loaded onto a tanker, will have at full strength both the well tank farm's code and the tanker's code. When it is off-loaded from the tanker into the refinery tank farm, the tanks in which it will be stored may contain oil with other earlier codes, as well as the tank farm code. This loading of the tanker's oil into a tank containing oil will dilute the tanker's code but, since all the oil in the tank farm contains the tank farm's code, there will be no dilution of the tank farm's jurisdictional code. Thus, in looking at a slick, one finds a predominant tag and tries to determine if there are other predominant tags. From one dominant tag an investigator can probably pick up a history of the oil and establish its absolute history by looking for other trace tags that would substantiate its origin. In all probability, a tanker spilling oil will have two dominant tags: one of the refinery and one of the tanker. And, obviously, the tags would indicate that the history of the oil was from the tank farm to the tanker. Jurisdiction would be assigned to the tanker unless there were extraordinary anomalies in other parts of the code pattern.

Cancellation of a code cancels jurisdiction, but not the material in the oil. For example, a tank farm oil will have its jurisdiction, or tag, canceled by the addition of a tanker code. The tank farm's code remains in the oil but the sequence of events, which can readily be established from the extensive records kept of oil shipments, will quickly show the responsible party. That is, tags will show recent jurisdictions but history will show last jurisdiction in case of ambiguity. In the profile system, cancellation of code profile is done by altering the profile. In any one jurisdiction the dominant code will be either that of the jurisdiction or a combination of jurisdictions and previous tank farm. This is because when oil is loaded onto a tanker there is seldom dilution, but during off-loading, dilution can occur or readily be arranged.

5.2.3.1 License Plate Tagging: In the first two examples which follow, oil is shipped from the well tank farms, labeled W, X, and Y, by tankers numbered 1 to 10, to the refineries labeled A, B, and C, and by the same tankers, 1 through 10, to the users labeled I, J, and K.

The oil passes through five jurisdictions: wells, tankers, refineries, back to tankers, and to users. Oil is tagged when it enters the well tank farms, when it enters the tankers, when it enters the refineries' tank farms, when it again enters the tankers, and finally when it is entered into the users' tank farms. This system can be extended to tag past the users, but five serialized taggings give the reader enough of an idea of the codes without being unduly complex.

Table 6 presents a code. The code contains 26 unique tags numbered 1 through 26. In reality the number of tags could be extended to hundreds or even thousands in number. Each tag position, i.e., 1, 2, 3, 4, ... 26 is a unique chemical or particle. In the code illustrated in table 6, tag number 1—in position 1—indicates that the oil has been tagged at a well tank farm; tag number 2—in position 2—indicates that the oil has at one time entered into the jurisdiction of a refinery tank farm. Tag number 3 indicates that the oil has been delivered to a user's tank farm, and tag number 4 indicates that the oil, at one point, has been shipped by a tanker. This information in these four positions gives a quick history of the oil. For example, if tags 1 and 4 are found, it means that the oil was shipped from the well tank farm via a tanker and then spilled.

The unique jurisdiction tagging, or "license plate" system, occurs after position 4. For example, tag 5 indicates that the oil was from well tank farm W; oil from well tank farm X has tag number 6 in it; oil from well tank farm Y has tag number 7 in it. Oil from tank farms 5, 6, and 7 will also have tag number 1 in the oil to indicate that it was from a well tank farm. Refinery oil from tank farms A, B, and C are tagged with tag numbers 9, 10, and 11, respectively, as their unique tags. This refinery oil is also tagged with tag number 2 to indicate that the oil has been delivered to a refinery tank farm at one point. Users' tank farms I, J, and K are tagged with material in position 13, 14, and 15, respectively. In addition, all oil in a user's jurisdiction will have tag number 3 to indicate that it has been in a user's tank farm.

TABLE 6

LICENSE PLATE TAGS

Tag Number	Jurisdiction
1	Well TF*
2	Refinery TF
3	User TF
4	Tanker
5	Well W TF
6	Well X TF
7	Well Y TF
8	Spare
9	Refinery A TF
10	Refinery B TF
11	Refinery C TF
12	Spare
13	User I TF
14	User J TF
15	User K TF
16	Spare
17	Tanker 1
18	Tanker 2
19	Tanker 3
20	Tanker 4
21	Tanker 5
22	Tanker 6
23	Tanker 7
24	Tanker 8
25	Tanker 9
26	Tanker 10

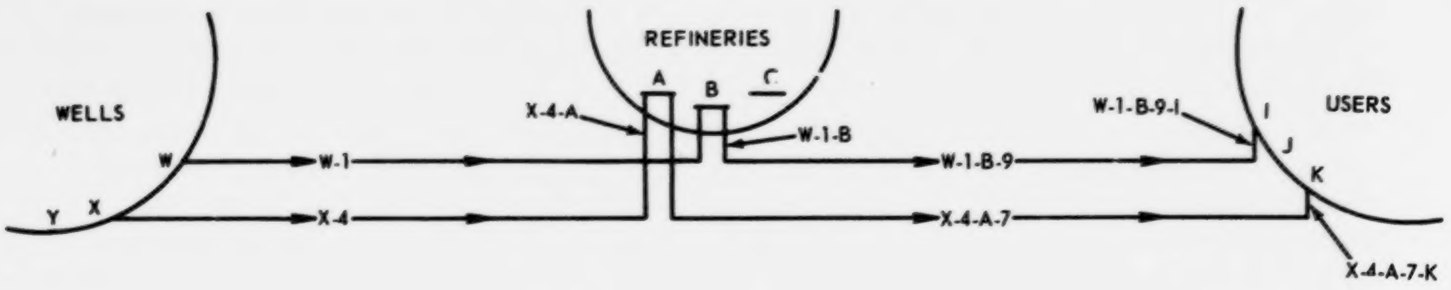
*Tank Farm

In this example, there are ten tankers, 1 through 10, that are tagged with unique tags, numbers 17 through 26, respectively. Also, the oil to all tankers will have tag number 4 to indicate that the oil has been carried in a tanker one or more times.

The upper part of figure 2 indicates the direction and code present in the oil as it passes from the wells to the refineries and finally to the user. To the left of center in figure 2 are the tanker codes, and, as explained in the previous paragraph, 4 means that the oil has been in a tanker, and 17 means that the oil is in tanker number 1. In a like manner, tanker number 8 is a 4:24 code; in this example, 4 means that it has been in a tanker, and 24 is the unique tag indicating that it has been in, or is in, the jurisdiction of tanker number 8. Well tank farm W has a 1:5 code, the 1 indicating that it is a well tank farm code and 5 being the unique code of that tank farm (W). Refinery tank farm C has a 2:11 code, 2 meaning that it has been in the jurisdiction of a refinery tank farm and 11 uniquely identifies with the refinery tank farm C. User tank farm J has a 3:14 code; 3 means it has been delivered to a user's tank farm and 14 is the unique code assigned to the tank farm J.

As the oil progresses from tank farm W to tanker number 1, to refinery B, back to a tanker—number 9—and finally to user I, the code, or "license plate," undergoes a number of changes. At the bottom of the page is a table indicating the code and the tags in the oil. W means tank farm W, W1 means it moved from tank farm W to tanker number 1, while W1B means the oil originated at tank farm W, was loaded into tanker number 1, and then off-loaded into the jurisdiction of tank farm B. Finally, code W1B9I means originating at tank farm W, shipped by tanker 1 to tank farm B, reshipped by tanker 9, and off-loaded to user tank farm I. Following the tags in the oil at tank farm W, it will have a 1:5 code, and after tanker 1 code, it will have a 1:4:5:17 code. When it is tagged with the refinery tank farm tag it will have a 1:2:4:5:10:17 code. And finally, in the user's tank farm W1B9I, it will have a 1:2:3:4:5:10:13:17:25 code. This code development can be seen at the bottom left of figure 2. In the example given, no dilution is assumed (the worst case). In the table at the right is the second example of oil originating at tank farm X, being shipped by tanker 4, being delivered to refinery A, being reloaded onto tanker 7, and being delivered to tank farm K at the user's terminal. In this case, it is assumed also that there is no dilution and that the tags remain unaltered in the residuum.

These codes are unique and can supply information about the history of the oil and of its jurisdiction. To the left of the double line at the bottom of figure 2, is the tagging license plate, or code, which contains the generic information: 1 meaning that the oil has been tagged at a tank farm associated with wells, 2 that it has been to a refinery, 3 that it has been delivered to a user, and 4 that the oil has been shipped by tanker. To the right of the lines are the unique jurisdictions.



TANKER NO.	CODE
1	4 17
2	4 18
3	4 19
4	4 20
5	4 21
6	4 22
7	4 23
8	4 24
9	4 25
10	4 26

WELL TANK FARM	CODE
W	1 5
X	1 6
Y	1 7

REFINERY TANK FARM	CODE
A	2 9
B	2 10
C	2 11

USER TANK FARM	CODE
I	3 13
J	3 14
K	3 15

JURISDICTION SEQUENCE				
W				
W	1			
W	1	B		
W	1	B	9	
W	1	B	9	I

CODE IN OIL AMPLITUDE DISREGARDED								
1				5				
1			4	5			17	
1	2		4	5	10		17	
1	2		4	5	10		17	25
1	2	3	4	5	10	13	17	25

JURISDICTION SEQUENCE					CODE IN OIL (AMPLITUDE) DISREGARDED								
X					1				6				
X	4				1			4	6			20	
X	4	A			1	2		4	6	9		20	
X	4	A	7		1	2		4	6	9		20	23
X	4	A	7	K	1	2	3	4	6	9	15	20	23

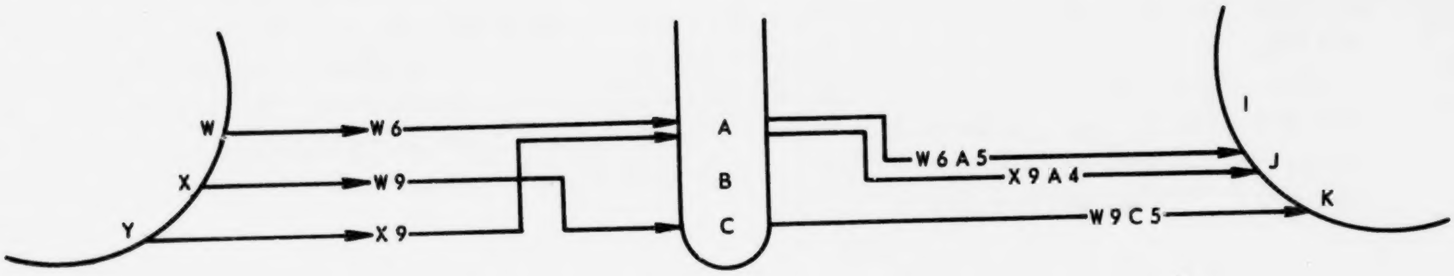
Figure 2. License Plate Coding Showing Oil from Wells W, X, Y Shipped to Refineries A, B, C and Reshipped to Users I, J, K by Tankers 1 through 10. (Well, Refinery, User, and Tank Codes are Shown. Actual Code in Oil as it Changes Jurisdiction is Shown in the Two Examples Above.)

In most spills, one or two at most, dominant tags will be present. However, to take a worst case, when tanker number 9 has jurisdiction of the oil and spills it, the dominant codes would be 10 and 25. It may very well be that 5 and 17 are present. One could see immediately, looking in the redundant information, that the oil has never been delivered to a user's destination and that it was picked up at a refinery on its way to some delivery point, by looking up the tanker code—25—which corresponds to tanker number 9. The only suspect is tanker number 9. By checking back in the records one can see readily that tanker 9 picked up oil from refinery B, thus canceling B's tag. Tanker 9 is the last jurisdiction and is legally responsible. Should the tanker captain argue that somehow his code was put accidentally into the oil, the question will arise as to how. If further arguments should arise, more careful analysis will reveal tags 5 and 17 present, which, even in this simple case, would uniquely identify the tanker run that was made.

5.2.3.2 Profile Tagging: In the profile method of tagging, a series of tags is added, which forms a profile in the oil. In this system, far fewer tags are required—less than a hundred. With a hundred tags, countless batches could be tagged. However, part of the code will be used to simplify analytical techniques.

In the following examples, a 12-bit tag is used which admits to 4096 unique tagging combinations. Part of the tag is a license plate tag which identifies, as in the previous example, whether the oil has been tagged at a well tank farm, a refinery tank farm, or a user's tank farm, or if it has been in a tanker. These positions are shown at the bottom of figure 3. In positions 5 through 12, an 8-bit tag, which allows 255 different combinations, is used to identify ten tankers, three well tank farms, three refinery tank farms, and three user tank farms. The routing is the same; that is, the oil goes from wells via tanker to refinery and thence forward via tanker to user. As in the previous example, well tank farms are identified by W, X, and Y, refineries by A, B, and C, and user tank farms by I, J, and K. Tankers are identified as 1 through 10. In figure 3, associated with each identifiable unit, is a binary code alongside the identifiable unit. The first four bits (see bottom of figure 3) of the binary code are really a use-unique code indicating the type of jurisdiction (e.g., well tank farm, refinery tank farm, user tank farm, or tanker) used in the tagging. This is the same as the first four bits in the license plate tagging system. The last eight places in the example are unique to the vehicle. Figure 3 shows the routing of the oil. The designation W6A5J is the same as in the previous example—that is, from tank farm W at the wells via tanker 6 to refinery A tank farm via tanker 5 to user J. Figures 4 through 8 (page 93) show the code profiles as the oil changes jurisdiction, and table 7 shows the binary codes in numerical tabular form corresponding to the profiles in the figures.

Figure 4A shows the profile code as added at tank farm X. Figure 5A is the profile at tank farm W as is figure 6A. Figure 7A shows also the code as added at tank farm W, but subsequent steps in 7 merely show the profile of the tagging code added for comparison to the historic codes containing tags from previous jurisdictions. Returning now to figure 4, the oil from the X tank farm is loaded onboard without dilution to tanker 9. Figure 4B shows the code profile with certain of the bits being


W
X
Y
W 6
W 9
X 9
A
B
C
W 6 A 5
X 9 A 4
W 9 C 5
I
J
K

TANKER NO.	TANKER PROFILE CODE											
1	0	0	0	1	0	0	0	1	1	1	0	1
2	0	0	0	1	0	0	1	0	0	0	1	1
3	0	0	0	1	0	0	1	1	1	1	0	0
4	0	0	0	1	0	1	0	0	1	0	1	0
5	0	0	0	1	0	1	0	1	0	1	0	1
6	0	0	0	1	0	1	1	0	1	0	0	1
7	0	0	0	1	0	1	1	1	0	1	1	0
8	0	0	0	1	1	0	0	0	1	0	1	1
9	0	0	0	1	1	0	0	1	0	1	1	1
10	0	0	0	1	1	0	1	0	1	1	1	0

WELL	CODE PROFILE											
W	1	0	0	0	1	0	0	1	1	1	0	0
X	1	0	0	0	0	1	0	1	1	0	1	0
Y	1	0	0	0	0	0	1	1	1	0	0	1
REFINERY												
A	0	1	0	0	1	1	0	0	0	1	0	0
B	0	1	0	0	1	1	0	1	1	0	1	1
C	0	1	0	0	1	1	1	1	1	1	0	0
USER												
I	0	0	1	0	1	1	0	1	1	1	0	1
J	0	0	1	0	1	1	1	0	1	0	1	1
K	0	0	1	0	1	1	1	1	0	0	0	0

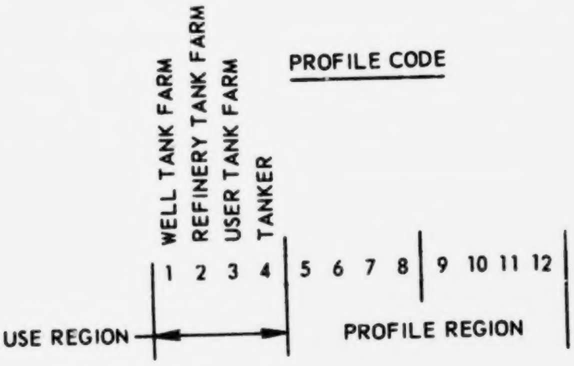

WELL TANK FARM
REFINERY TANK FARM
USER TANK FARM
TANKER
PROFILE CODE
1 2 3 4
5 6 7 8
9 10 11 12
USE REGION
PROFILE REGION

Figure 3. Profile Code with Same Wells, Refineries, Users, and Tankers, Using a Binary Code (Note that Positions 1 through 4 Denote a Use While Positions 5 through 12 in Profile Region Denote Tanker.)

twice the normal height common to both the tank farm and the tanker code. When the oil in tanker 9 is off-loaded to tank farm A, it is assumed to undergo a dilution of ten to one and the resulting code profile is shown in figure 4C. Some background tag noise will be added to oil being diluted—not shown in this example—but it is not important because the dominant profile is that of the added code. Also, it is the profile, not the dominant profile, that counts in this system. In figure 4D the oil is loaded back onto a tanker, number 4, and the resulting profile can be seen. Trace amounts of other codes still remain which cause minor variations in the profile. In figure 4E the ten-to-one dilution occurs when the oil is unloaded into tank farm J of the user. The very low values of the certain bits, such as those in position 2, 4, 8, and 10, are the results of this dilution.

Figures 5 and 6, showing the origin of different oil shipped by overlapping routes, are used to illustrate the difference in profile that results when there are differences in commonality. For example, figures 4C and 5C are both in the same jurisdiction and their profiles are quite similar except for minor perturbations. However, figure C is in a different refinery and the profile is very different. Figures 4D and 5D are in different tankers and have different profiles but they have been both unloaded to J and, therefore, figures 4 and 5E are quite similar. Figures 5C and 6C are in different refineries and, therefore, look quite different, but are then loaded onto the same tanker and, due to the back tagging of the two different refineries, the tag profiles look different. Both can be identified, however, and, with a little information processing, can be shown to have been in tanker 5. They unload at different terminals, so the two codes are different and can be shown to be different.

Figure 7 is simply the profile of the code that is introduced at the point of loading for figure 6. It can be shown that these profiles look fairly similar to the profiles in the oil by comparing figure 7 to figure 6. As previously pointed out, however, this can be misleading and it takes a little more sophisticated code reading to uncover the differences.

The code in figure 6 differs from the codes in figures 4 and 5 because at every step of tagging a ten-to-one dilution occurred. Thus, the code profile in figure 7 is created by a situation which would more resemble the bunkering of merchant marine ships. It is difficult to conceive how the tank farm code could be diluted ten to one when loading on a tanker. On the other hand, it is possible to have a tanker code ten times as concentrated as a tank farm code so, essentially, loading on a tanker is equivalent to dilution. Figure 8 is assuming the ten-to-one dilution on off-loading a tanker into a tank farm. The constraints in figure 8 are the same as those in figures 4 and 5, but the code in figure 8 is identical to the code in figure 6, with different dilution constraints. The relative profile differences may be seen. Table 7 shows the computed codes for each one of the steps. In the rows are the code profiles and in the extreme left-hand corner is the actual coding history. To the right of the code index, such as in the upper left-hand corner, the code for figure 4 is X9A, followed by a symbol 10 indicating division by ten. This means that the previous codes are assumed to have undergone a ten-to-one dilution. In the code for figure 6 there are four ten-to-one dilutions in a row, and, as explained earlier, this is why figure 8 compares so closely to figure 7 in code profiles.

With the profile system, when a spill occurs there will be a history of tankers in the immediate area. By comparing the anticipated coding profiles with the various tankers, a large percentage of the tankers can be eliminated by vacant bit position analysis. For example, in figures 4D and 5D, the 11-place bit is vacant in 5D but occupied in 4D. This means that if tankers 4 and 5 traversed the same path, loaded with oil from refinery A, and a spill occurred, tanker 5 would be eliminated from a possibility of having the spill. However, tanker 4, under the analysis of this one-bit place, would be a potential candidate as author of the spill.

However, elimination of a tanker is not enough to convict another tanker of guilt. Here the quality-control samples taken at the time of tagging would be brought to bear. Upon elimination of all tankers whose code profiles are simply not compatible with the spilled profiles, the choice between several would have to be made. By obtaining the quality-control sample taken at the time of tagging and comparing this profile to the tanker profile, a one-to-one correspondence should be obtainable. In this case, it is a stable fingerprint of tagged material, which will then do for the conviction. The profile code system requires that, not only should a tag be identified as present, but also, its magnitude be known within some percentage which depends on the dilution ratios.

5.2.4 Summary and Conclusions

To obtain a conviction via the tagging process, it is necessary to use tagged oil. Two methods have been proposed and both will be satisfactory. It is believed that the individual license plate technique for the larger system is more satisfactory, but, for immediate tagging purposes, profile-chemical tagging is probably simpler. There is ample material to tag all the necessary jurisdictions.

Mixtures of oil spills comprise a more difficult problem. In a spill containing only two sources of tags in about equal proportions, both systems can clearly distinguish between the two spillers and assess a roughly proportional guilt. The "license plate" method is more explicit in this case. However, when there is a ten-to-one mixture (ten parts of one party and one part of another), finding the minor spiller becomes more difficult. There will be times when this can be done and there may very well be times when there is too much ambiguity. At the present time, it is not known how many multiple spills have occurred. In fact, use of a tagging system should provide the first evidence for or against this phenomenon. The authors believe, however, that multiple spills occur rarely and are of little consequence; should a tagging system be put into effect, they would be so rare as to seldom be a problem in the assessment of guilt.

Because of the problem of tag interaction and masking from one jurisdiction to the next as well as the ambiguities in spill mixtures, one central body should control the tagging code and the amounts added, at least in the initial stage of the development of oil tagging. Envisioned is a bonded service group serving the oil industry by devising codes for each jurisdiction, and doing quality control work and analysis of spill mixtures. Outside laboratories could check analyses for the establishment of court information in legal cases. However, for general quality control work and system improvement one control group would be essential as the tagging system is expanded.

TABLE 7

NUMERICAL VALUES CORRESPONDING TO FIGURES 4, 5, 6, AND 8

Code for figure 4

Dilution												
X	1	0	0	0	0	1	0	1	1	0	1	0
X9	1	0	0	1	1	1	0	2	1	1	2	1
X9A ÷ 10	0.1	1	0	0.1	1.1	1.1	1.0	1.2	1.1	1.1	0.2	0.1
X9A4	0.1	1	0	1.1	1.1	2.1	1.0	1.2	2.1	1.1	1.2	0.1
X9A4J ÷ 10	0.01	0.1	1	0.11	1.11	1.21	1.1	0.12	1.21	0.11	1.12	1.01

Code for figure 5

Dilution												
W	1	0	0	0	1	0	0	1	1	1	0	0
W6	1	0	0	1	1	1	1	1	2	1	0	1
W6A ÷ 10	0.1	1	0	0.1	1.1	1.1	1.1	1.1	1.2	1.1	0	0.1
W6A5	0.1	1	0	1.1	1.1	2.1	1.1	2.1	1.2	2.1	0	1.1
W6A5J ÷ 10	0.01	0.1	1	0.11	1.11	1.21	1.11	0.21	1.12	0.21	1.0	1.11

TABLE 7

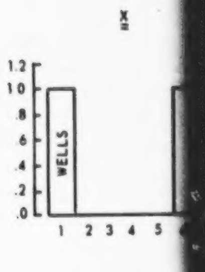
NUMERICAL VALUES CORRESPONDING TO FIGURES 4, 5, 6, AND 8 (Continued)

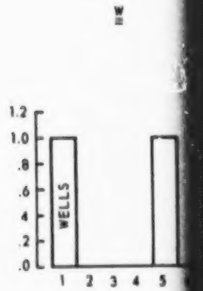
Code for figure 6

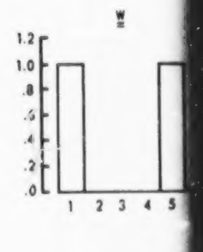
	Dilution												
W		1	0	0	0	1	0	0	1	1	1	0	0
W9	÷ 10	0.1	0	0	1	1.1	0	0	1.1	0.1	1.1	1	1
W9C	÷ 10	0.01	1	0	0.1	1.11	1	0	0.11	0.01	1.11	0.1	0.1
W9C5	÷ 10	0	0.1	0	1.01	1.111	1.1	0	1.01	0	1.111	0.01	1.01
W9C5K	÷ 10	0	0.01	1	0.1	1.01	1.11	1	1.1	0	0.11	0	0.1

Code for figure 8

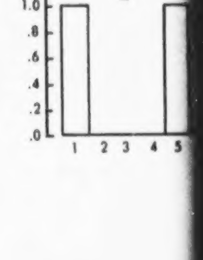
	Dilution												
W		1	0	0	0	1	0	0	1	1	1	0	0
W9		1	0	0	1	2	0	0	2	1	2	1	1
W9C	÷ 10	0.1	1	0	0.1	1.2	1	0	0.2	0.1	1.2	0.1	0.1
W9C5		0.1	1	0	1.1	1.2	1	0	1.2	0.1	2.2	0.1	1.1
W9C5K	÷ 10	0.01	0.1	1.0	0.11	1.12	1.1	1.0	1.12	0.01	0.22	0.01	0.11

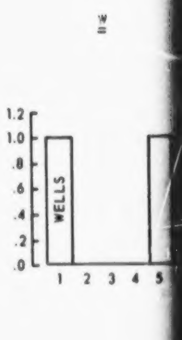






Figures 4 through 8 show profile codes in oil for each jurisdiction. In figure 4 the oil moves from jurisdiction X, to 9, to A, to 4, and finally to user J. In figure 5C the oil has moved from Tank Farm W by Tanker 6 to Refinery A. Note, therefore, that 4 and 5C have the same jurisdiction and similar profiles. Likewise, figures 4 and 5E have been moved by a different tanker to User J and have similar profiles. Figures 6, 7, and 8 are the same jurisdiction across the page but with different ratios. In figure 6, at each jurisdictional change, a 10:1 dilution is assumed. Figure 7 is step-by-step with a profile of the added code. And comparing 7 to 6 shows the similarity of code profiles in the case stated. Figure 8 assumes a 10:1 dilution entering Tank Farm associated with Tank Farms and Users but no dilution on entering Tanker. Consequently, figures 8B and D have different profiles from 6B and D and 7B and D. But profiles in 6, 7, and 8C and E are quite similar. Profile distortions based on dilution are easily handled anlytically.





A

NOTE DOUBLE UNDERSCORES OF LAST FIGURES INDICATE WHO HAS JURISDICTION.

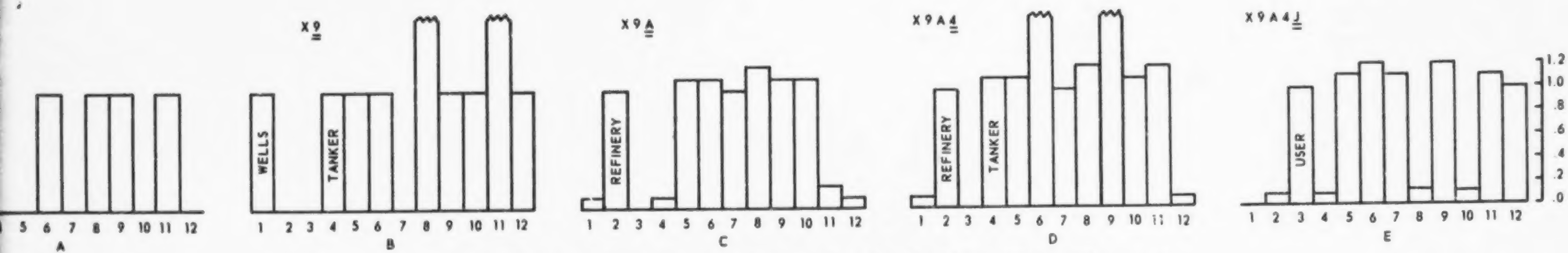


Figure 4. Profile Codes in Oil from Jurisdiction X to User J

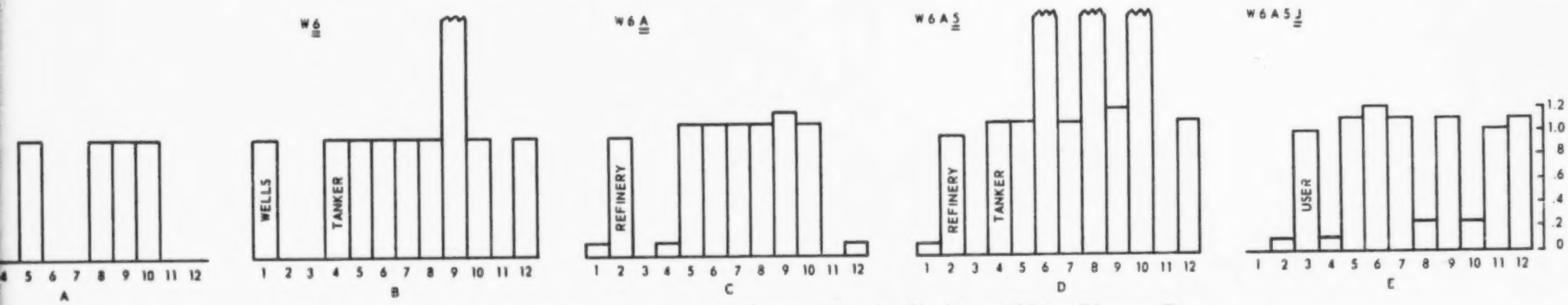


Figure 5. Profile Codes in Oil from Jurisdiction W to User J

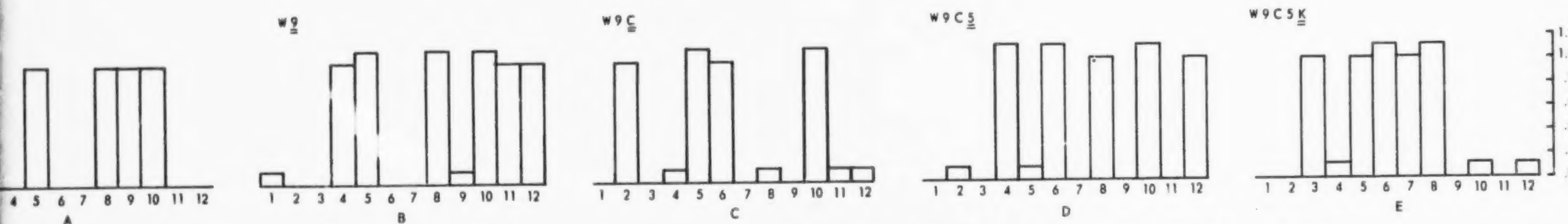


Figure 6. Profile Codes in Oil Showing a Ten-to-One Dilution at Each Jurisdictional Change

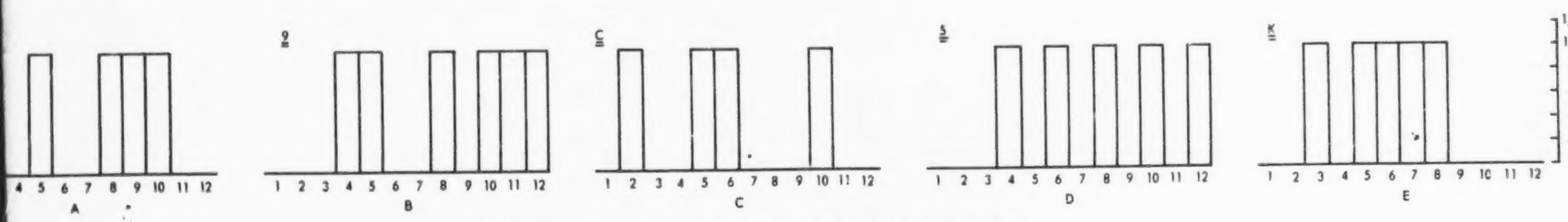


Figure 7. Profile of the Added Code

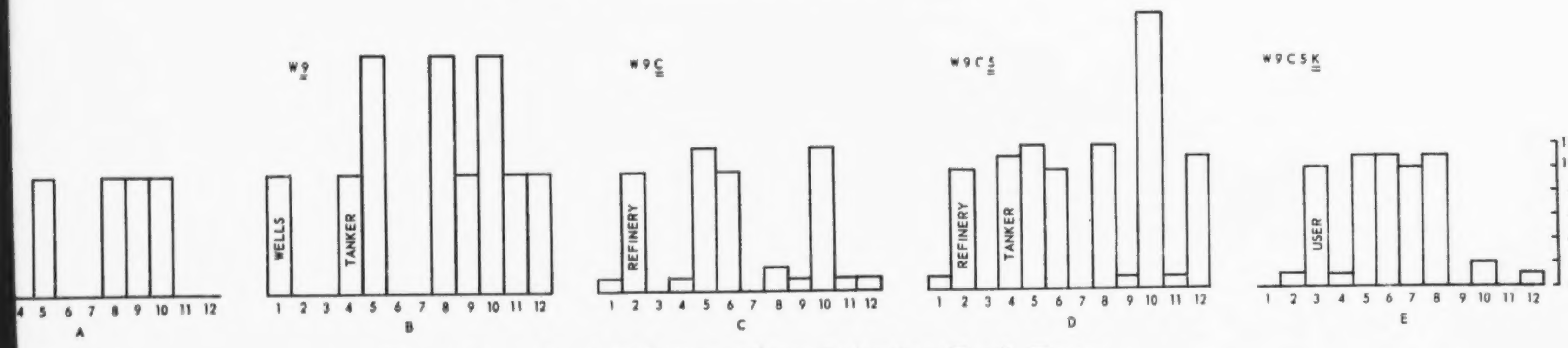


Figure 8. Code Dilution when Entering Tank Farm

B

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

There are several thousand oil spills on U.S. waters each year; only a small fraction of these are reported to the authorities. In view of this situation, it is desirable to be able to identify (by analyzing oil slicks) those who are responsible for oil spills.

There are two approaches to identification: passive tagging and active tagging. Passive tagging is a convenient circumlocution for no tagging at all: Nothing is added to the oil; the slick itself must provide all the evidence for its identification. Active tagging involves adding some known and readily identifiable material to the oil. The added material must satisfy several criteria: It must be soluble or dispersible in oil and insoluble and nondispersible in water; it must be chemically and physically stable in both spilled and unspilled oil; and it must not interfere with the commercial uses of petroleum. One additional criterion: It must not be too expensive. Two figures of speech are helpful in distinguishing active tagging from passive tagging: Passive tagging amounts to a "fingerprint," active tagging amounts to a chemical or physical "license plate."

Passive tagging is not at all attractive, for the fingerprint is very likely to be changed or to be washed away as the slick is exposed to the abundant sources of chemical and physical energy in the sea and sky. The easily identifiable passive tags of petroleum (e.g., isotope ratios, trace metals) cannot be assumed to be stable in the slick — indeed, there is little doubt that they are unstable — and the more stable passive tags in the slick (e.g., heavy aromatic and alkylaromatic hydrocarbons) are prohibitively difficult to separate and identify. In short, fingerprinting seems neither technically feasible nor scientifically valid.

Active tagging, however, offers several attractive possibilities. It appears that making a good license plate is much easier than finding a good fingerprint. We have examined two types of active tags: oil-soluble tags (organometallics and halogenated polycyclics) and particulate tags (coded microspheroids). Several very attractive organometallics have been developed by the National Bureau of Standards in conjunction with the American Petroleum Institute; they seem to have all the properties of good active tags (compatibility with oil, insolubility in water, chemical and physical stability, ease of identification), and they are sold by the Bureau for $2.00 a gram. We strongly recommend that pilot studies of oil tagging be conducted with these organometallics. The halogenated polycyclics also have desirable properties, and it would be well to subject a few candidates from this class to preliminary feasibility tests. Although the feasibility of particulate tags has not yet been demonstrated, coded microspheres appear to have exceptional promise: Many are already commercially available at very low prices; an astronomic variety of coded microspheroids can be made easily and inexpensively by custom synthesis; and all the particulate tags can be quickly separated from samples of slick and readily identified by available analytical techniques.

SECTION VII

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ABSTRACT

Several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques; and it must have no adverse effect on the oil's subsequent use. Three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three

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Melpar, a division of American-Standard, Oil Tagging System Study, FWPCA Contract No. 14-12-500, May 1970.

ABSTRACT

Several methods of identifying the source of oil pollution are critically examined. These methods are grouped into two categories: passive tagging and active tagging. Passive tagging assumes that oils are so chemically diverse that their contents constitute a stable chemical fingerprint that can be unequivocally disclosed in the laboratory. Active tagging requires that an inexpensive, coded material be added to oil; this material must be chemically and physically stable in both oil and oil slicks; it must also be readily identifiable by available analytical techniques; and it must have no adverse effect on the oil's subsequent use. Three methods of passive tagging (trace metals, sulfur-isotope ratios, and paper chromatography) and three

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methods of active tagging (halogenated polycyclic aromatics, organometallics, and coded microspheroids) have been examined. Passive tags cannot be recommended because the passive tags are quite likely to mingle, to evaporate, to be dissolved, or to be oxidized; even if these processes do not occur, they can create formidable forensic problems for the prosecution and telling counter-arguments for the defense. Since active tags are designed to be stable and identifiable, they are satisfactory for the job; and the three types of active tags reviewed show promise and merit.

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